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PROCEEDINGS OF THE SECOND INTERNATIONAL SYMPOSIUM ON PHOSPHOGYPSUM

VOLUME I

GREAT SEAL OF THE STATE OF FLORIDA
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Organized by
The University of Miami
under a grant sponsored by the
Florida Institute of Phosphate Research
Bartow, Florida

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FLORIDA INSTITUTE OF PHOSPHATE RESEARCH

The Florida institute of Phosphate Research was created in 1978 by the Florida Legislature {Chapter 378.101, Florida Statutes) and empowered to conduct research supportive to the responsible development of the state's phosphate resources. The institute has targeted areas of research responsibility. These are: reclamation alternatives in mining and processing, including wetlands reclamation, phosphogypsum storage areas and phosphatic clay containment areas; methods for more efficient, economical and environmentally balanced phosphate recovery and processing; disposal and utilization of phosphatic clay; and environmental effects involving the health and welfare of the people, including those effects related to radiation and water consumption.

FIPR is located in Polk County, in the heart of the central Florida phosphate district. The institute seeks to serve as an information center on phosphate-related topics and welcomes information requests made in person, by mail, or telephone.

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Organized by
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DISCLAIMER

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The demand for improved agricultural production to provide adequate food supplies for the world's growing population has called for every increasing levels of phosphate fertilizer production. And since the majority of the phosphate fertilizers used today are derived from wet process phosphoric acid, the question of "what to do with the by-product phosphogypsum" has assumed ever increasing importance.

Various environmental concerns have also contributed to the growing interest in achieving environmentally acceptable means of utilizing this abundant raw material. The past decade has seen curtailments in phosphogypsum ocean dumping and with this practice under increased attack worldwide, the time is rapidly approaching when this disposal method will likely be prohibited. In parts of the world such as China, no new phosphoric acid capacity can be built unless the facility is equipped to convert all the phosphogypsum produced into salable (disposable off site) products. The loss of hundred of acres of agricultural land for non-productive phosphogypsum storage is considered too great a price to pay for increase phosphate production. In the U.S. a recommendation that the phosphate complexes along the Mississippi River be allowed to dump phosphogypsum into the river has met with much opposition.

At the same time, the concept that phosphogypsum is "just a waste product" that can only be stacked up in ever growing piles has begun to change. Today’s phosphate producers are beginning to accept phosphogypsum as a potentially valuable raw material for agricultural uses, construction applications, and as a source of sulfur for chemical processes producing sulfuric acid and even elemental sulfur. The combination of environmental concerns and potentially profitable uses is certain to influence the speed with which methods to utilize phosphogypsum are adopted.

The International Symposiums on Phosphogypsum provide a forum and a meeting place where both researchers and active practitioners in phosphogypsum utilization have the opportunity to discuss the latest developments with these people who are acutally doing the work. This informal one-on-one exchange of information is probably equally as important as the formal program presentations.

Solving the "phosphogypsum problem" is not an impossible goal. The solution will most likely consist of a number of economical applications with no one all around solution adopted universally. The basis for solving this problem may well have been recorded in this publication of the papers presented at the "Second International Symposium on Phosphogypsum." It is hoped that this publication will encourage increased investigation of this "problem" and that the "solution(s)" will prove to be near at hand.

KEYNOTE ADDRESS

THE FLORIDA INSTITUTE OF PHOSPHATE RESEARCH; A UNIQUE RESEARCH ORGANIZATION

Jeremy A. Craft
Chief, D.N.R. - Bureau of Mine Reclamation
and
Chairman, Board of Directors
Florida Institute of Phosphate Research

Government influences research in many ways. The most obvious way is through the operation of universities thereby providing for all types of pure and applied research in an academic atmosphere. Another way is by providing monetary incentives for research in government programs such as the space program. Government may also force research. For example, the U. S. Environmental Protection Agency developed standards based on best management practices which in effect were technology forcing standards. E.P.A. forced the implementation of experimental technology in an effort to achieve theoretical results in pollution control.

I am here this evening to discuss another, rather unique, means by which government influences research. The Florida Institute of Phosphate Research, the sponsor of this symposium is a unit of the State of Florida. The Institute is funded entirely from a portion of the severance tax paid by the phosphate mining industry in Florida. The Institute was established in 1978 for the purposes of conducting research into problems of the phosphate industry in the areas of mining, reclamation, beneficiation, chemical processing, and radiation. One idea behind the Institute is that it can study problems which are too large and costly for individual companies to study. The study of phosphogypsum is one clear example of a problem in the industry that needs a consolidated effort of study.

The Institute has committed approximately $22,000,000 to research since 1978. Approximately one third of this has been spent on phosphogypsum studies which have been identified by the Institute to be of the highest priority. The Institute's budget for this fiscal year is approximately $8,000,000. In addition to research in all major areas of responsibility, the Institute is spending $1,000,000 to conduct a survey of radon throughout Florida by measuring radon levels in approximately 7,000 homes. We are also spending close to a million dollars to conduct a feasibility study for the mining of Lake Hancock, a 4,000 acre, highly polluted, lake. The Lake Hancock study is designed to address the feasibility of restoring the environmental quality of the lake considering mining and reclamation as one alternative.

The Institute has complete laboratory facilities available for those conducting research in phosphate. We have contracted for the construction of two new buildings and a green house to aid in this research. We have already committed approximately $7,000,000 for the continuation of research projects presently underway.

As Dr. David Borris stated earlier, there are approximately one billion tons of phosphogyspum in the world. Approximately 30% of this is located in Florida. The Florida Institute of Phosphate Research is committed to solving what is not just a Florida problem but a worldwide problem. To this end, we have identified phosphogypsum research as our number one priority and we are committed to sharing our findings through technology transfer programs such as this.

We have a saying in this country that "what is one man's junk is another man's treasure." As we become more and more aware of the earth's limited resources and available lands, you as research scientists must carry the challenge to turn this "junk" we call phosphogypsum into a "treasure."

ENVIRONMENTAL ISSUES

RADIOLOGICAL ASSESSMENT OF THE APPLICATION OF PHOSPHOGYPSUM TO AGRICULTURAL LAND

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ABSTRACT

There is considerable interest in the application of phosphogypsum to agricultural land. Since this material contains the naturally-occuring radium-226 and its decay products lead-210 and polonium-210, it is important to evaluate the extent to which the radioactivity would appear in crops and contribute to human radiation exposure.

This paper explores the methodology for assessing this radiological impact, reviews literature reports, and examines the the availablility of necessary input data.

As an example case, an assessment was performed for the application of phosphogypsum at the rate of 1 ton/acre (0.224 kg/m^2) once every four years to land used for grain crops. It was concluded that there is no significant radiological problem associated with the conduct of this practice for decades. For application periods beyond 50 years, the conclusions depend upon factors not well defined. The technique can be used for evaluating other application and cultivation scenarios, additional radionuclides, and/or other crops. Efforts should be directed toward obtaining the data needed as input for more definitive assessments.

INTRODUCTION

There is considerable interest in, and some precedent for, the use of phosphogypsum as a soil conditioning agent and/or source of supplemental calcium and sulfur (Lloyd, 1985). Since phosphogypsum contains naturally-occuring radionuclides of the uranium decay series, it is important to evaluate the extent to which this radioactivity would appear in crops and contribute to human radiation exposure. This work explores the methodology for assessing this radiological impact, reviews literature reports, examines the availability of the necessary data, and, as a test case, assesses the impact of radium-226 from the application of phosphogypsum to land used for grain crops.

THE RADIOACTIVITY OF PHOSPHOGYPSUM

Uranium and its decay series are associated with phosphate deposits of marine origin. Uranium-238 is the first member of a l6-member radioactive series (Figure 1). In phosphate rock, the various members of this series are in approximate radioactive equilibrium (i.e., present in equal radioactivity concentrations). Upon acidulation in the wet-process phosphoric acid chemical plant, the equilibrium is disrupted and there is a redistribution of the radioactivity, Most of the uranium, thorium, and

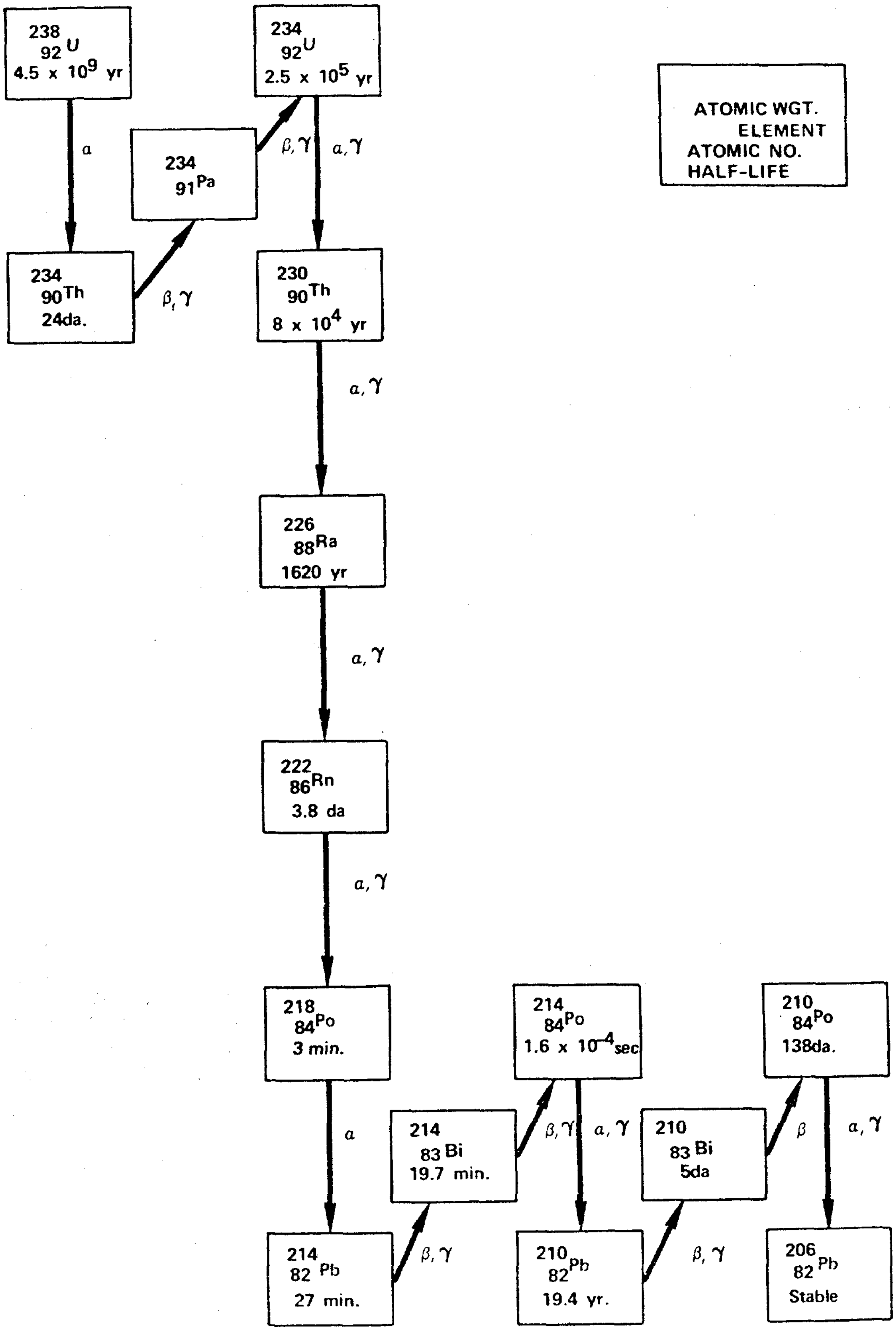

Figure 1. Uranium Decay Series

lead-210 appear in the phosphoric acid while radium-226, being chemically similar to calcium, favors the phosphogypsum. Polonium-210 also appears in the phosphogypsum, However, tile concentrations initially expected in the fresh byproduct will decrease with the 138-day half-life characteristic of this radionuclide.

The decay of radium-226 in the phosphogypsum will result in the formation and reappearance of subsequent members of the decay series. In the absence of further separation processes, radioactive equilibrium eventually will be re-established. The ingrowth of radon-222 and decay products through polonium-214 will be governed by the 3.8-day half-life of radon-222; the rate of ingrowth of the subsequent decay products will be governed by the 22-year half-life of lead-210. The ratio of the concentrations of lead-210 and its decay products to the concentration of radium-226 will be 50% in 22 years, 75% in 44 years, etc.

Three of the radionuclides expected in phosphogypsum are potentially significant from an agricultural standpoint. Radium-226 is a long-lived (1600-year half-life) alpha emitter that follows chemical and biological pathways similarly to calcium. Polonium-210 is an alpha emitter and hence a potential hazard inside the body. In the absence of lead-210 it would not be persistent since its half-life is only 138 days. The beta-emitting lead-210 is less of a hazard itself; however, it is mobile biologically and serves as a persistent production source for polonium-210.

Typical radionuclide concentrations for Central Florida phosphate rock and phosphogypsum derived from that rock are shown in Table 1. Concentrations in phosphogypsum from other sources would be expected to be in proportion to the concentrations in the input rock.

RADIOLOGICAL ASSESSMENT METHODOLOGY

The assessment of the ultimate radionuclide intake by humans and resulting radiation dose from a practice involving the application of a radioactivity-bearing material to agricultural land involves the following steps:

1. Define application conditions,
2. Estimate resulting additions to soil radioactivity,
3. Estimate radionuclide uptake by plants and resulting concentrations in food products,
4. Model radionuclide intake by humans and resulting radiation dose, and
5. Compare results to criteria and standards.

This sequence is summarized in Table 2. Many of the factors used as input are unique to the specific material, radionuclide, application scenario, and crop. A further explanation of the assessment methodology is available on request from the author.

Table 1. Typical Concentrations of Radioactivity in Central Florida Phosphate Matrix, Rock, and Phosphogypsum

Material, Radionuclide	Concentration		Notes
	pCi/g	kBq/kg	
Matrix:			a)
Radium-226	38 (18-84)	1.4 (0.7-3.1)	c), d)
Pebble:			b)
Radium-226	57 (44-97)	2.1 (1.6-3.6)	c), d)
Concentrate:			b)
Radium-226	37 (26-51)	1.4 (1.0-1.9)	c), d)
Phosphogypsum:			b)
Uranium-238,234	4	0.15	e), f)
Radium-226	26	1.0	e), f)
Lead-210	Initially	low	g)
Polonium	40	1.5	h)

Notes:

a) Concentrations in North Florida matrix are approximately 25% of those for Central Florida.

b) Concentrations in North Florida products are approximately 50% of those for Central Florida.

c) The uranium series will be approximately in radioactive equilibrium in materials prior to the chemical plant.

d) From Roessler, et al. (1979).

e) From Guimond and Windham (1975).

f) From May and Sweeney (1982).

g) Lead-210 concentrations will be low in fresh phosphogypsum but will increase as lead-210 is produced by decay of radium-226. The ingrowth process is governed by a 22-year half-life - i.e., lead-210 concentration/radium-226 concentration will be about 0.4 in 22 years, 0.75 in 44 years, etc.

h) Polonium-210 concentrations estimated on the basis of the report by Hurst (1982) that from phosphate rock with radium-226/polonium-210 equilibrium, 60% of the radium-226 and 99% of the polonium-210 appeared in the gypsum.

Table 2. Procedure for Radiological Assessment of the Application of Radioactivity-bearing Material to Agricultural Land

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1. **Define Application Conditions:**

   a) Material to be applied - description, kinds and quantities of radioactivity.
   b) Application scenario - amount per application; frequency.
   c) Cultivation practice - depth of tilling after application.
   d) The crop.
   e) Expected pathways to humans -
      i) direct consumption (for vegetables, fruit, food grains)
      ii) consumption of animal products (when the crop is animal forage or feed grain).

2. **Estimate Additions to Soil Radioactivity**

   a) Calculate activity added per application.
   b) If the scenario involves more than one application:
      i) determine annual rate of application, and
      ii) determine cumulative concentration resulting from continued application.

3. **Estimate radionuclide Uptake by Plants and the Resulting Concentrations in Food Products**

   a) Using soil-to-plant transfer factors, model the uptake by plants, estimating the concentration in food or animal feed portions.
   b) If an animal feed crop, estimate transfer from animal feed to the human food product (meat, dairy products, or eggs).

4. **Model Radionuclide Intake by Humans and the Resulting Radiation Doses**

   a) Estimate radionuclide intake (from appropriate dietary model).
   b) Calculate the corresponding radiation doses (from a dosimetry model).

5. **Compare Intakes and Doses to Criteria and Standards**

   a) Soil radioactivity (from step 2).
   b) Concentration in food commodities (from step 3).
   c) Radionuclide intake (from step 4).
   d) Radiation doses (from step 4).

REPORTED ASSESSMENTS

While there are numerous instances of the application of phosphogypsum and other radium-bearing materials to agricultural lands, there are only a few radiological assessments in the literature.

Lindekin and Coles (1978) reported a radiological assessment for the application of phosphogypsum to vegetable crop land. For a scenario of ten 0.66 kg/m^2 applications of phosphogypsum containing 15 pCi/g radium-226 (mostly North Florida rock), tilled to a 15-cm depth, they calculated a soil radium addition of 0.45 pCi/g. Using a concentration ratio of 0.056 (dry-weight basis), they predicted a concentration in vegetables of 0.025 pCi/g and projected that a 50-yr vegetable consumption of 400 g/day (wet weight) or 80 g/day (dry weight) would result in a 50-yr integrated dose to the bone of 160 mrem. They concluded that "there is little basis for concern regarding a radiological hazard from the uptake of radium-226 by plants grown on phosphogypsum treated soils".

In another assessment considering application initially at 10 ton/acre and subsequently at 5 ton/acre on alternate years, and a 15-cm till depth, Lindekin (1980) concluded it would take more than 100 years before the soil radium content built up to 5 pCi/g. Using a plant/soil concentration ratio of 0.01 (dry weight basis) and a consumption of 80 g/day (dry weight), he predicted a radium intake from vegetables grown on this soil of 4 pCi/day. For continuous consumption over a period of 50 years, this would result in an integrated radiation dose to the surface of the bone of 1.4 rem.

In the preceeding examples, soil radium buildup was probably overestimated because it was assumed that there was no radium washout (leaching) or depletion via uptake by crops grown on the soil. In turn, the plant radium uptake was probably also over-estimated due to the soil radium overestimate, the fact that radium sulfate has a low solubility, and the expectation that excess calcium in the gypsum would reduce radium uptake by plants. It should also be noted that these assessments assumed that the consumer's entire vegetable intake was from this land and did not include any dilution from other food sources.

A report by Golden (1983) on the application of phosphogypsum to sugarcane lands included actual radioactivity analyses. Radioactivity was detected in the phosphogypsum but after application of 1 ton/acre, the radioactivity of the treated soil was not significantly different from that of untreated (check) plots. Neither treated nor check plot cane juice samples had radioactivity concentrations significantly different from background. However, while the radioassay instrumentation and method were not described in the report, it appears that the methods used were not as sensitive as current state of the art. Thus this study should be considered only as an indication that there was no evidence of major radionuclide uptake.

Assessments have been made of the application of other radium-bearing materials to agricultural land. Owen and Hyder (1980) cite a literature report of an instance where chlorinator residues from the production of zirconium metal had a radium-226 concentration of 500 pCi/g. Sludge from the settling ponds at the facility was applied as a soil conditioner to test plots at the rate of 76 metric tons/ha (34 tons/acre) and 448 metric tons/ha (200 tons/acre). While elevated radon flux measurements over these plots were indicative of elevated soil radium, rye grass showed no significant uptake of radium. Unfortunately, this report does not indicate the sensitivity of the radioanalytical method.

As a matter of comparison, most phosphate fertilizers based on superphosphates also contain radium-226. Guimond (1978) notes that potato, sugarcane, tobacco, and tomato fields have annual P_2O_5 applications of more than 200 lbs/acre, and calculates that 250 lbs/acre adds 0.02 pCi/g radium-226. He indicates that, since radium is strongly absorbed (sic) in the soil, radium losses would be primarily sediment erosion and should be similar to phosphate loss which is in the range of 0 to 60% over many years. He then concludes that over 50 years, the radium-226 buildup due to fertilizer use might be up to 1 pCi/g, depending upon fertilizer type. This may be compared to the 0.5 to 1 pCi/g considered as the typical radium-226 content of U.S. soils. Davis, et al. (1979), also evaluate the effect of radium-226 in fertilizer. For four major crops, cotton, soybeans, corn, and wheat, they cite average and maximum P_2O_5 application rates of 31.8 and 200 lb/acre, respectively. Applied in the form of normal superphosphate containing 21.3 pCi/g radium-226 (112 pCi/g P_2O_5), a single year's application increases the soil radium content by 0.0018 pCi/g and 0.011 pCi/g in the average and maximum application cases, respectively. By taking ratios to the average naturally-occuring soil radium concentration and the average population dose due to radium, they conclude that these soil radium additions correspond to additional endosteal cell (bone surface) radiation doses of approximately 0.018 mrem/yr (average application) and 0.11 mrem/yr (maximum application).

EXAMPLE CASE - RADIUM-226 IN GRAINS

Consider for an example case, radium-226 resulting from the application of phosphogypsum to land used for grain production. For this assessment it is assumed that the radium-226 concentration of the phosphogypsum has an upper limit value of 30 pCi/g. Maximum application rates are projected to be 1 ton/acre (0.224 kg/m^3 with an application frequency of no more than once per four years. For the purpose of this assessment, it is assumed that the soil is tilled to a depth of 15 cm (6 in) and that the grains are directly consumed by humans in the form of grain, cereals, flour, meal, etc.

SOIL RADIOACTIVITY

An application of 0.224 kg/m^2 of material with a radium-226 content of 30 pCi/g adds 0.672 pCi/cm^2 (6,720 pCi/m^2). If this application occurs once every 4 years, this corresponds to an annual rate of 0.168 pCi/cm^2-yr (1,680 pCi/m^2-yr).

Additions to soil radium-226 concentration are summarized in Table 3. Assuming uniform mixing through a till depth of 15 cm and a soil density of 1.5, a single application results in an addition of 0.030 pCi/g. If continued, this practice corresponds to an annual application rate of 0.0075 pCi/g-yr.

Table 3. Radium-226 Addition to Soil Through Application of Phosphogypsum

	Radium-226
PROJECTED FOR PHOSPHOGYPSUM APPLICATION:(a)	
Addition from single application	0.03 pCi/g
Application rate for repeated applications every 4 years	0.0075 pCi/g-yr
Cumulative addition, application every 4 years:	
- 50-yr application, no removal	0.38 pCi/g
- Equilibrium value, 2% removal/yr	0.37 pCi/g (b)
- Equilibrium value, 0.1% removal/yr	5.3 pCi/g (c)
COMPARISON DATA:	
Single Additions:	
- Superphosphate fertilizer use, average application rate	0.002 pCi/g (Davis, et al., 1977)
- Superphosphate fertilizer use, maximum application rate	0.01 pCi/g (" ")
- From criteria for land application of water treatment sludge	0.1 pCi/g (IDNS, 1984)
Application Rates	
- Superphosphate fertilizer use, average application rate	0.002 pCi/g-yr (Davis, et al., 1977)
- Superphosphate fertilizer use, maximum application rate	0.01 pCi/g-yr (" ")
- From criteria for land application of water treatment sludge, 0.1 pCi/g every 3 years	0.033 pCi/g-yr (IDNS, 1984)
Soil Radium Concentration:	
- Typical natural soil radium	0.5 - 1 pCi/g (NCRP, 1984)
- NCRP guideline for restricting use for human food crops	40 pCi/g (NCRP, 1984)

Notes:

(a) Application assumptions: 0.225 kg/m^2 (1 ton/acre), 30 pCi/g, 15-cm (6-inch) till depth, 1.5 g/cm^3 soil density.

(b) For 2% removal/yr, 90% equilibrium requires 100 years.

(c) For 0.1% removal/yr, 90% equilibrium requires 1600 years.

The cumulative effect of long-term continued practice is more difficult to assess. The length of time over which it would be beneficial to continue the application has not been defined and loss rates due to causes other than radioactive decay are a major uncertainty. Consequently, several scenarios were considered.

If there were no losses of radium-226 from the till layer, 50 years of this practice would contribute:

0.0075 pCi/g-yr X 50 yrs = <u>0.375 pCi/g</u>.

This 50-year projection has two oversimplifications; it does not consider the effect of continuing use beyond 50 years, and it assumes soil radium concentration continues to increase linearly without any losses.

For a 2% per year loss of radium-226 from the root zone, the equilibrium concentration would be 0.37 pCi/g; 90% of equilibrium would be achieved in 100 years. For loss rates of less than 2%/yr, equilibrium concentrations will be higher but the times to reach equilibrium will also be longer. For example, with a loss rate of 0.1% per year, continuation of the practice for thousands of years will eventually result in an equilibrium concentration addition of <u>5.3 pCi/g</u>. With no removal other than radioactive decay, the model predicts an equilibrium concentration of 18 pCi/g after thousands of years.

UPTAKE BY CROPS

The uptake of radium-226 by grains grown on the phosphogypsum-treated land was predicted by use of soil-to-plant transfer factors from the literature. A transfer factor of 1.0 (pCi/g fresh plant per pCi/g dry soil) was selected as a conservative value (Roessler, 1987). In addition, an upper limit to the radium-226 concentration in grain was imposed. Based on field observations with other radium-bearing materials, the maximum concentration in grain under continued phosphogypsum application to the soil should not exceed 0.25 pCi/g (Roessler, 1987).

Predicted radium-226 concentrations in grain are summarized in Table 4 for several scenarios. For a <u>single application</u> to the soil, the predicted incremental radium concentration in grain is:

0.03 pCi/g X 1.0 = <u>0.03 pCi/g</u>.

For the selected scenarios of <u>continued application</u>, it would be <u>0.25 pCi/g</u>.

INTAKE BY HUMANS

Intake can be derived from concentration if a model is specified for the consumption of the particular food commodity. Two cases were considered, the "sole-source" case in which 100% (200 g/day) of the grain and grain-product intake comes from phosphogypsum-treated land and the "cosmopolitan diet" case in which 10% (20 g/day) of these food products comes from phosphogypsum-treated land.

Table 4. Predicted Radium-226 in Grain from Land Application of Phosphogypsum

Scenario	Concentration pCi/g
PROJECTED FOR PHOSPHOGYPSUM APPLICATION: (a),(b)	
1. Single Application	0.03
2. 50-yr Application, no removal, (0.38 pCi/g soil radium)	0.25
3. Equilibrium values, continuous application, 2% removal/yr, (0.37 pCi/g soil radium)	0.25
4. Equilibrium values, continuous application, 0.1% removal/yr, (5.3 pCi/g soil radium)	0.25 (c)
TYPICAL U.S. VALUES (McDowell-Boyer, et al., 1979):	
Rice	0.00029 to 0.002
Grain and Grain Products	0.0022 to 0.0025

Notes:

(a) Application assumptions: 0.225 kg/m^2 (1 ton/acre), 30 pCi/g, 15-cm (6-inch) till depth, 1.5 g/cm^3 soil density. Single application gives 0.03 pCi/g. Repeated applications every 4 years; equivalent to 0.0075 pCi/g-yr.

(b) Grain concentration based on plant (fresh wt.)/soil (dry wt.) transfer factor = 1.0.

(c) Upper limit to grain concentration set at 0.25 pCi/g (see text).

As indicated in Table 5, incremental intake estimates range from 0.6 to 50 pCi/day, depending upon the diet assumption and the gypsum application scenario used. For the single phosphogypsum application/cosmopolitan diet scenario, the projected radium-226 intake is:

0.03 pCi/g X 20 g/day = 0.6 pCi/day.

The projected increases in radium intake were calculated in a similar fashion for the other scenarios.

RADIATION DOSES

Two types of dose were computed, the dose to the bone surfaces and the committed effective dose equivalent (CEDE). The bone surface represents the individual tissue receiving the greatest radiation dose from the intake of radium-226. Bone surface doses were calculated using a factor of 6 mrem/yr per pCi/day intake (NCRP, 1984). The CEDE expresses the effect of an intake in terms of the effective uniform whole-body dose presenting the same cumulative risk as the actual non-uniform irradiation delivered by the radionuclide. This concept allows direct comparisonand summing of the effects of various radionuclides that may have different distributions in the body, follow different biological turnover rates and/or be characterized by different sets of significantly irradiated tissues. CEDE's were calculated using a factor of 0.0011 mrem/pCi intake; this is derived from factors in ICRP Report 30 (ICRP, 1979).

For the single application/cosmopolitan diet scenario, doses are:

Bone surface: 0.6 pCi/day X 6 mrem-day/pCi-yr = 3.6 mrem/yr, and
CEDE: 0.6 pCi/day X 365 days/yr X 0.0011 mrem/pCi = 0.24 mrem/yr.

Doses were calculated in a similar fashion for the other scenarios. Radiation doses are presented in Table 6 for the various intake projections.

DISCUSSION

The predicted additions to soil, crop, dietary radium-226 and the resulting radiation doses are summarized in Table 7.

Soil Radioactivity

While the 0.03 pCi/g radium-226 addition by a single phosphogypsum application exceeds that expected from a single superphosphate fertilizer application, the addition (a) meets the 1 pCi/g criterion established for water treatment sludge, (b) represents an increment that is only 3 to 6 % of the 0.5 to 1.0 pCi/g concentrations typically present in the soil and is small relative to the variations in the normal background concentration, and (c) results in a soil concentration well below the 40 pCi/g NCRP guideline for restricting use for human food crops. Thus, a single application has a minimal impact on soil radium concentration.

Table 5. Projected Radium-226 Intake by Consumers of Grain from Phosphogypsum-treated Land

Scenario	Predicted Intake pCi/day
PROJECTED FOR PHOSPHOGYPSUM-TREATED LAND:	
Single Application: (a)	
- Cosmopolitan diet (b)	0.60
- Sole-source diet (c)	6.0
Continued Application: (d)	
- Cosmopolitan diet	5.0
- Sole-source diet	50
COMPARISON DATA:	
Typical U.S. intake (NCRP, 1984)	1 - 2
Basis for the Drinking Water Standard	10
Federal Radiation Council guidance	20

Notes:

(a) Single phosphogypsum application adds 0.03 pCi/g to soil radium-226. Projected increase in grain is 0.03 pCi/g.

(b) Cosmopolitan diet - 10% of grain and grain product intake (20 g/day) comes from phosphogypsum-treated land.

(c) Sole-source diet - 100% of grain and grain-product intake (200 g/day) comes from phosphogypsum-treated land.

(d) Continued application: applications every 4 years; equivalent to 0.005 pCi/g-yr. Upper limit on grain concentration, 0.25 pCi/g.

Table 6. Projected Radiation Dose to Consumers of Grain from Phosphogypsum-treated Land

Scenario	Radiation Dose, mrem/yr	
	Bone Surface (a)	CEDE (b)
PROJECTED FOR PHOSPHOGYPSUM-TREATED LAND:		
Single Application: (c)		
- Cosmopolitan diet (d)	3.6	0.24
- Sole-source diet (e)	36	2.4
Continued Application: (f)		
- Cosmopolitan diet	30	2.0
- Sole-source diet	300	20
COMPARISON DATA:	Whole-body Dose Equivalent mrem/yr	
Individual dose limit, releases from nuclear facilities	25 (EPA, 1985)	
NCRP recommended limit for individual of the general public:		
- continuous exposure	100 (NCRP, 1984)	
- exposure in any one year	500 (NCRP, 1984)	

Notes:

(a) Bone surface dose based on 6 mrem/yr per pCi/day intake (or 0.016 mrem/pCi intake) (NCRP, 1984).

(b) CEDE = Committed Effective Dose Equivalent.
Based on 0.0011 mrem/pCi intake, derived from ICRP Report 30 values (ICRP, 1979).

(c) Single phosphogypsum application adds 0.03 pCi/g to soil radium-226. Projected increase in grain is 0.03 pCi/g.

(d) Cosmopolitan diet - 10% of grain and grain product intake (20 g/day) comes from phosphogypsum-treated land.

(e) Sole-source diet - 100% of grain and grain-product intake (200 g/day) comes from phosphogypsum-treated land.

(f) Continued application: applications every 4 years; equivalent to 0.0075 pCi/g-yr. Upper limit on grain concentration, 0.25 pCi/g.

Table 7. Summary of Radiological Impacts of Application of Phosphogypsum to Agricultural Lands - Example Case: Grains.

Effect	Single Application	Application Every 4 Years
Soil radium-226, pCi/g (a)	0.03	0.38, 0.37, 5.3
Radium-226 in grain, pCi/g (b)	0.03	0.25
Radium-226 intake, pCi/day:		
- cosmopolitan diet (c)	0.6	5
- sole-source diet (d)	6	50
Bone surface dose, mrem/yr: (e)		
- cosmopolitan diet	3.6	30
- sole-source diet	36	300
Committed Effective Dose Equivalent, mrem/yr: (f)		
- cosmopolitan diet	0.24	2.0
- sole-source diet	2.4	20

Notes:

(a) Application assumptions: 0.224 kg/m^2 (1 ton/acre), 30 pCi/g phosphogypsum, 15-cm (6-in) till depth, 1.5 g/cm^3 soil density. Repeated applications every 4 years , equivalent to 0.0075 pCi/g-yr. Repeated application scenarios include 50-yr application with no removal (0.38 pCi/g in soil); application to equilibrium with 2%/year removal (0.37 pCi/g in soil), and application to equilibrium with 0.1% /yr removal (5.3 pCi/g in soil).

(b) Grain concentration based on plant (fresh wt.)/soil (dry wt.) Concentration ratio = 1.0. Upper limit on grain concentration set at 0.25 pCi/g (see text).

(c) Cosmopolitan diet - 10% of grain and grain product intake (20 g/day) comes from phosphogypsum-treated land.

(d) Sole-source diet - 100% of grain and grain-product intake (200 g/day) comes from phosphogypsum-treated land.

(e) Bone surface dose based on 6 mrem/yr per pCi/day intake (or 0.016 mrem/pCi intake) (NCRP, 1984).

(f) Committed Effective Dose Equivalent based on 0.0011 mrem/pCi intake, derived from ICRP Report 30 values (ICRP, 1979).

While the average annual radium-226 addition of 0.0075 pCi/g-yr under continued phosphogypsum use every fourth year is about four times that from average superphosphate fertilizer practice (Davis model), this addition rate is less than that from maximum superphosphate fertilizer practice and 23% of that from triennial application under the water treatment sludge criterion. Thus, the average annual application rate of 0.0075 pCi/yr is intermediate among rates from other, existing practices.

The cumulative addition of 0.38 pCi/g for the 50-year/no-loss scenario is 38% of the 1 pCi/g projection by Guimond (1978) for 50 years application of superphosphate at the annual rate of 250 lbs P 05/acre. The resulting soil radium concentration is on the order of 38% to 76% higher than the natural concentration of 0.5 to 1.0 pCi/g but only about 3% of the NCRP criterion of 40 pCi/g. This is a detectible increase in soil radium, but the value lies within the range of variations in the normal background concentration and does not exceed any existing guidelines or criteria for radium in soil or soil amendments.

Projections of effects for longer time periods are more speculative. For the model used, the ultimate concentration and the approach to a steady state depend upon the loss rate from the till zone, a factor that is not well defined. Indefinite application could result in concentrations significantly greater than projected for the 50-yr practice. However, to reach cumulative additions of 1 or more pCi/g would require hundreds of years. The extremely long-term, equilibrium scenarios are not likely to be achieved in practice. A significant fraction of the soil would consist of phosphogypsum and it is likely that the optimum benefits to crop production would have been reached and the effect on crop production would limit the practice long before such a radium concentration is reached.

Uptake by Crops, Intake by Humans, and Radiation Dose

McDowell-Boyer, et al. (1979) report typical values of 0.29 to 2.0 pCi/kg (0.00029 to 0.002 pCi/g) for rice and 2.2 to 2.5 pCi/kg (0.0022 to 0.0025 pCi/g) for other whole grain products. If radium-226 concentrations in grain actually reached 0.25 pCi/g following continued application of phosphogypsum to soil, this concentration would be significantly higher than reported for typical grains and grain products. The value of 0.25 pCi/g is ten times the average value and four times the maximum value observed in grains grown on reclaimed phosphatic clay containing 20 pCi/g of radium-226 (Roessler, et al., 1986). These observations suggest that the 0.25 pCi/g upper limit to the concentration in grain, and hence the corresponding intakes and doses, are conservative on the high side; however, there are no direct experimental data for these crops and phosphogypsum to corroborate this statement.

There is no standard for radioactivity in food items other than drinking water. Rather, the significance of radioactivity in individual food items must be evaluated on the basis of the resulting radioactivity intakes by humans and of the associated radiation doses.

The 0.6 pCi/day projected radium-226 intake for the single phosphogypsum application/cosmopolitan diet scenario is 60% of the estimated typical U.S. dietary intake for that radionuclide and is probably within the variation in that estimate. This intake is 6% of the intake corresponding to the EPA Drinking Water Standard and 3% of Federal Radiation Council (FRC) intake guidance. The corresponding CEDE of approximately 0.2 mrem/yr is well below the uncertainty in the estimation of background radiation. Thus, the predicted 0.03 pCi/g contribution to the radium-226 content of grain would have a minimal impact on the cosmopolitan diet.

The projected 5 to 6 pCi/day radium-226 intakes from the single application/sole-source and the continued application/cosmopolitan diet scenarios are about 5 - 6 times the estimated typical dietary intake. They represent 50 - 60% of intake under the drinking-water standard and 25 - 30% of the FRC intake guidance. The corresponding approximately 2 mrem/yr CEDE's are one to two orders of magnitude below the criteria given, Thus, impacts are limited for these scenarios. While the projected incremental radium intakes are several times the typical U.S. dietary intake, they meet available intake criteria.

It is inherent to the definition of the two diet models that the intakes and doses are a factor of ten higher for the sole-source diet than for the cosmopolitan diet. For the continued application/sole-source diet scenario, The 50 pCi/day projected intake is about 50 times the typical daily dietary intake. This intake is about five times that under the drinking water standard and 2.5 times the FRC intake guidance. The corresponding 20 mrem/yr CEDE is a substantial fraction of the average background radiation dose, is 20% of the NCRP recommendation for continuous exposure to an individual of the general public and approaches the 25 mrem/yr EPA limit for emissions from individual nuclear facilities. For this scenario, the projected intakes and doses are significant. However, the sole-source diet is probably not a realistic model. In fact, it seems extremely unlikely that an individual would derive even 10% of his total grain products (such as bread, flour products, cereals and other grain products) from phosphogypsum-treated land.

In performing this assessment, assumptions were used that were believed to be conservative on the high side with respect to concentration, intake, and dose.

OTHER FOOD PRODUCTS, CROPS, AND RADIONUCLIDES

If the crops were to be used for animal feed, the route of intake by humans would be via meat, dairy products, and/or eggs rather than directly-consumed grain products. In such a case, the intakes and doses for humans would be significantly lower than for direct consumption of grain.

An assessment for other crops would require appropriate soil-to-plant transfer factors for the crop and dietary intake quantities for the resulting food products; it would then proceed in a fashion similar to the grain example.

For other radionuclides such as lead-210 and polonium-210, the assessment would be conducted in a similar fashion. However, fewer data are available for transfer factors and typical concentrations.

CONCLUSIONS AND RECOMMENDATIONS

1. The assessment of the radiological impact of the application of phosphogypsum to agricultural land would be facilitated by a better definition of input conditions. In particular, these include:

   a) better definitions of the continued application scenario for projection of the long-term cumulative concentration in the soil, and
   b) better specification of the dietary role of the candidate crops or their products.

2. Further research is needed on uranium-series radionuclide behavior. There is a need for a better understanding of:

   a) the behavior of radium-226 and its decay products in phosphogypsum-treated soil, and
   b) the uptake by plants of radium and decay products from phosphogypsum.

3. With regard to the specific case of radium-226 and grain products, it is concluded:

   a) there is no significant problem associated with the proposed application of phosphogypsum to grain crop lands for periods up to tens of years,

   b) for application periods beyond 50 years, the conclusions are dependent upon factors that are not well defined, and

   c) if it is agronomically desireable to continue the practice for longer periods of time, an experimental and field testing program should be set up to obtain the data needed to perform a more definitive long-term assessment.

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REFERENCES

Davis, W., Jr., F.F. Haywood, J.L. Danek, R.E. Moore, E.B. Wagner, and E.M. Rupp. 1979. Potential Impacts of Recovery of Uranium from Wet-process Phosphoric Acid. ORNL/EPA-2, Oak Ridge National Laboratory, Oak Ridge, TN.

EPA. 1985. National emmision standards for hazardous air pollutants. Part 61, Code of Federal Regulations, Title 40, U.S. Environmental Protection Agency. Sup. of Documents, U.S. Gov. Printing Office, Washington, DC.

Golden, L.E. 1983. The effect of soil application of radioactive by-product gypsum on sugarcane yield and radioactivity of soil and sugarcane juice. Soil Fertility and Nutrition Studies with Sugarcane in Louisiana. Louisiana Agricultural Experiment Station, Baton Rouge. Agronomy Research Report #78: 38-42.

Guimond, R.J. and S.T. Windham. 1975. Radioacitvity Distribution in Phosphate Products, By-products, Effluents and Wastes. U.S. Environmental Protection Agency Tech Note ORP/CSD-75-3.

Guimond, R.J. 1978. The radiological aspects of fertilizer utilization. Radioactivity in Consumer Products, U.S. Nuclear Regulatory Commission, Washington, DC. NUREG/CP-0001: 380-393.

Hurst, F.J. and W.J. Arnold. 1982. A discussion of uranium control in phosphogypsum. Hydrometallurgy. 9: 69-82.

ICRP. 1979. International Commission on Radiological Protection. Limits for intake of radionuclides by workers. ICRP Report 30, Part I. Annals of the ICRP. 3: Pergamon Press, Oxford.

IDNS. 1984. Management of Water Treatment Plant Sludge Containing Elevated Levels of Radium. Illinois Department of Nuclear Safety, Springfield, IL.

Lindeken, C.L. 1981. Radiological considerations of phosphogypsum utilization in agriculture. Phosphogypsum (Proceedings of the International Symposium on Phosphogypsum), Publication No. 01-0001-018: 59-480. Florida Institute of Phosphate Research.

Lindeken; C.L. and D.G. Coles. 1978, The radium-226 content of agricultural gypsums. Radioactivity in Consumer Products. U.S. Nuclear Regulatory Commission Report NUREG/CP-0001: 369-375.

Lloyd, G.M. Jr. 1985. Phosphogypsum, a review of the Florida Institute of Phosphate Research programs to develop uses for phosphogypsum. Publication No. 01-000-035. Florida Institute of Phosphate Research.

May, A. and J.W. Sweeney. 1982. Assessment of Environmental Impacts Associated with Phosphogypsum in Florida. Bureau of Mines Report of Investigations 8639.

McDowell-Boyer, L.M., A.P. Watson, and C.C. Travis. 1979. Review and Recommendations of Dose Conversion Factors and Environmental Transport Parameters for ^{210}Pb and ^{226}Ra, NUREG/CR-0574 ORNL/NUREG-56 U.S. Nuclear Regulatory Commission, Washington, DC.

NCRP. 1984. Exposures from the Uranium Series with Emphasis on Radon and Its Daughters. Report 77, National Council on Radiation Protection and Measurements, Bethesda, Maryland.

Owen, P.T. and L.K. Hyder. 1980. Technologically Enhanced Natural Radiation: An Overview. ORNL/CF-80/265, Oak Ridge National Laboratory, Oak Ridge, TN.

Roessler, C.E., Z.A. Smith, W.E. Bolch and R.J. PRince. 1979. Uranium and radium-226 in Florida phosphate materials. Health Physics. 37: 269-277.

Roessler, C.E., J.G. Wood, and M. Shavers. 1986.Unpublished data; University of Florida, Gainesville, FL 32611,

Roessler, C.E. 1987. Review of bases for radiological assessment of the agricultural use of phosphogypsum - radium-226/grain crop case. Unpublished, available upon request from author. University of Florida, Gainesville, FL 32611.

RADON EMANATION FROM BUILDING MATERIALS

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ABSTRACT

Working with the Phosphate Institute of the University of Miami, we have investigated phosphogypsum wall panels for use in the construction industry. Phosphogypsum, however, contains radium in levels elevated from normal background. Radium decays radioactively into radon which is a radioactive, inert gas. Our interest has been focused on the problem of radon emanation into a structure constructed with phosphogypsum.

We have measured radon levels in a structure constructed from phosphogypsum panels and correlated these levels with various environmental parameters, It was observed that the radon emanation depended strongly on temperature and relative humidity. Furthermore, in the case of a windowless, single room structure with minimal air circulation, average radon concentrations in the structure approached the maximum values recommended by the State of Florida. In order to inhibit radon emanation into the structure, we subsequently investigated coating the panels. Several possible coatings were tried and it was found that radon emanation could be reduced by more than 95 percent.

INTRODUCTION

The Phosphate Research Institute of the University of Miami has constructed a test structure from panels composed of a phosphogypsum mixture. Phosphogypsum, a by-product of the phosphate industry, contains a somewhat elevated concentration of $radium^{226}$ (25 to 30 pCi/gm compared to background levels of 0.2 to 2.0 pCi/gm). $Radium^{226}$ decays to $radon^{222}$, a radioactive noble gas. A potentially hazardous situation arises if the radon can diffuse from its matrix before it decays (half life of 3.83 days) since it, in turn decays through a series of daughters which are not gaseous. These daughters can be deposited in the bronchial epithelium if the radon is inhaled.

The test structure represents a 'worst case' situation since it is a single closed room and the panels containing the phosphogypsum had been painted on the outside only. Over a period of several months, we measured average radon levels with type SF track etch detectors (Terradex Corp., Glenwood IL) and instantaneous radon levels with an RGA-400 radon gas analyzer (EDA Instruments, Toronto Canada). The instantaneous measurements were correlated with several environmental parameters. The radon levels, measured with the track etch detectors ranged from 3.16 to 4.82 pCi/l with a mean of 3.8 pCi/l (1). This is very close to the value of 0.02 working levels (WLs) recommended by the State of Florida as a maximum interior concentration.

In an effort to reduce the radon levels in the test structure, we have investigated several coatings that can be painted onto the interior walls of the structure. These coating materials have been painted onto several test panels and the relative radon flux has been measured using charcoal canister detectors.

MATERIALS AND METHODS

Details of the construction of the fully enclosed test structure have been documented elsewhere (Medora, 1986). The structure can be summarized as being a rectangular room approximately 2 x 4 meters in size, and 2.5 meters high. It has a single door but no windows. The structure is mounted on a trailer and is raised about 1.5 meters above ground level with a clear air space under the trailer. The panels for the walls, floor and roof were constructed using a mixture of 50% phosphogypsum, 25% cement and 25% sand reinforced with galvanized steel wire mesh. Each unit consists of a sandwich of two panels separated by a polystyrene core.

Radon levels in the structure were measured in two ways. A continuous sampling instrument (RGA-400) was used to obtain instantaneous (averaged over 30 minutes) values of both radon and radon daughter concentrations in the structure. This instrument uses surface barrier detectors and multichannel analyzers to measure the concentrations in air that is continuous1y pumped through the housing. It provides time varying data for periods up To several weeks . However, absolute calibration of the system is difficult and therefore, these data are used to provide relative information only . The temperature, atmospheric pressure and relative humidity in the structure were measured concurrently with the radon levels using analog instrumentation that produced chart records of these parameters as a function of time.

Integrated values of radon concentration (averaged over periods of one to several months) were obtained using the track etch detectors. These detectors incorporate filters to remove radon daughters and the decay of the radon gas reaching the cellulose nitrate film is recorded by tracks which are rendered visible by the etching process. These detectors are accurately calibrated by Terradex and provide absolute values of the radon concentrations in units of pCi/l. Working levels have been approximated by using a working level ratio of 0.5 (Stranden et al., 1979).

In order to measure the relative radon emanation from panels that have been coated with different materials, we have constructed a number of detectors that utilize the ability of charcoal to adsorb radon on its surface. The charcoal is placed in a metal canister 7.5 cm in diameter and 5.5 cm deep. A bed of 6 x 16 activated charcoal, 2 cm deep is placed in each can. About 46.5 gm of charcoal is used for each detector. A small vent hole, 0.5 cm in diameter is cut in the top of the can to maintain pressure equilibrium. Before use, the canisters are purged by heating in an oven at 90 degrees Celsius for one day.

After removal from the oven, the detector background is established by counting it with a NaI scintillation detector mounted in a low background shield and connected to a multichannel analyzer. The canister is then cemented to the phosphogypsum panel and exposed for a period of 25 hours. Following exposure, the canister is removed, sealed and allowed to equilibrate for a period of 4 hours before counting. This allows the growth of radon daughters. Although the absolute quantities of radon emitted by the panels during the collection time are small, the detector systems are sufficiently sensitive to allow measurements of the relative permeability of the various coatings.

The calculation of radon flux using the above experimental method involves two basic assumptions. First, we must assume that the charcoal is 100% efficient in the collection of radon for short time periods. Hartley and Freeman (1986), have shown that this assumption is good for periods up to 36 hours. The second assumption is that the radon flux being measured is constant over the time period. Our previous measurements of radon levels in the phosphogypsum structure imply that this assumption is not true since radon emanation depends on many environmental parameters that change over the course of the day. However; we are primarily interested in the relative radon emanation from several panels so that the above deviation from ideal behavior is irrelevant provided the data is not used to imply absolute values of flux.

Radon flux can be calculated (Hartley and Freeman, 1986) from the equation:

$$J = \frac{CL^2}{KAE[1-e(-Lt_1)][e(-L(t_2-t_1)) - e(-L(t_3-t_1))]} \qquad (1)$$

where: J = radon flux, pCi/m^2sec

C = net counts under ^{214}Bi, 609 keV peak

L = radon decay constant, 2.097 E-6 /sec

A = area of collector, m^2

K = conversion from d/sec to pCi, 0.037 d/sec/pCi

t_1 = exposure time, sec

t_2 = time from start of measurement to start of counting, sec

t_3 = time from start of measurement to end of counting, sec

In any experiment, all of the above parameters are kept constant so that the relative radon flux will be directly proportional to the ratio of the net counts under the ^{214}Bi, 609 keV peak. That is

$$\frac{J_1}{J_2} = \frac{C^1}{C_2} \qquad (2)$$

This is the basic principle used to compare the radon flux from various panels.

Once the above ratio has been determined for a given coating material, it is possible to estimate the change in the radon concentration in the test structure when it is painted on the inside. If the radon flux from a panel is known, the contribution to the radon concentration in the structure, from the panel, can be calculated (Jonassen, 1977) from the equation:

$$C = \frac{L}{L+n} \cdot J \cdot \frac{S}{V} \qquad (3)$$

where: L = the decay constant of radon n = air exchange rate

J = radon flux

S = inside area of the room

V = volume of the room

If the air exchange rate, temperature, humidity, pressure and other environmental conditions remain constant, for different radon fluxes, we have

$$\frac{C_1}{C_2} = \frac{J_1}{J_2} \qquad (4)$$

With this method, we can estimate the change in radon concentration in the structure once it has been painted.

RESULTS

Figure 1 shows the relative, diurnal variation of the radon levels in the test structure. It can be seen that these levels vary by as much as a factor of 10 over the course of a day. We

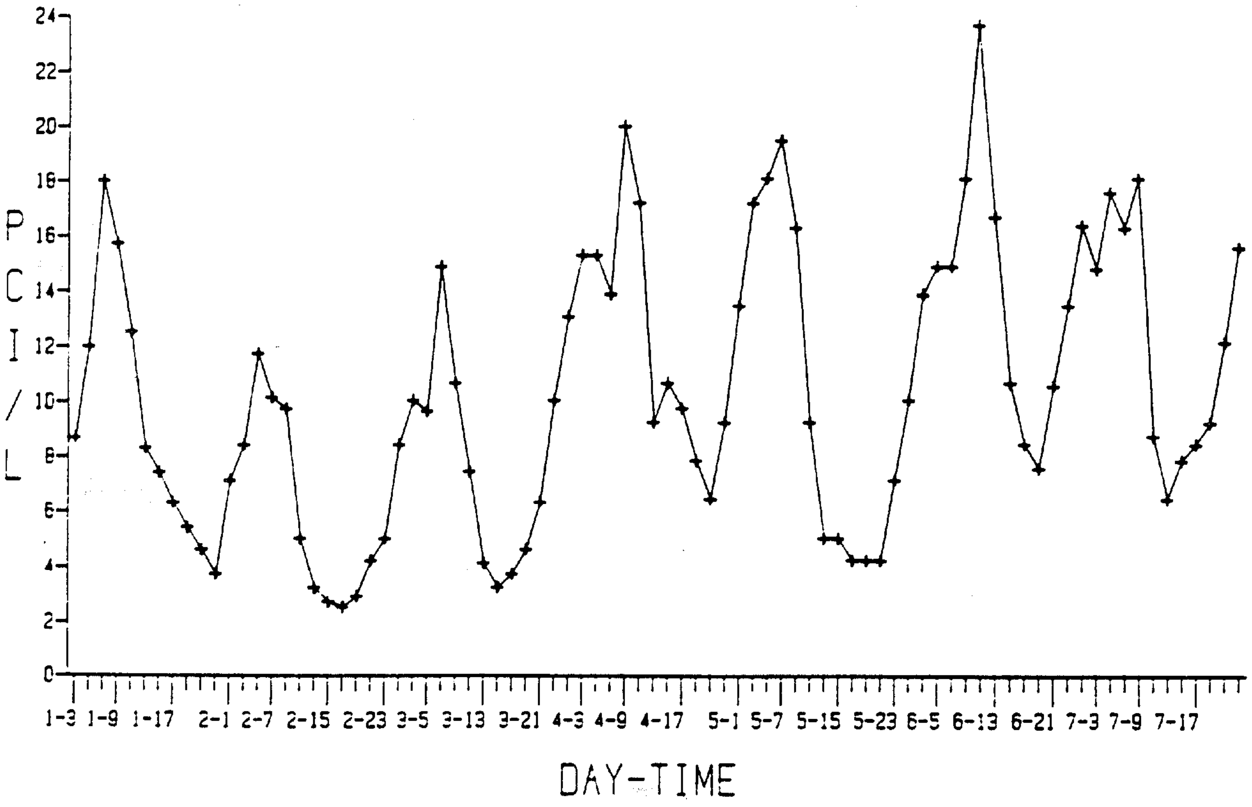

Fig.1. Diurnal Variation of Radon Gas Concentration (pCi/l).

have attempted to isolate the dependence of this variation upon several environmental parameters. Figure 2 shows the variation of

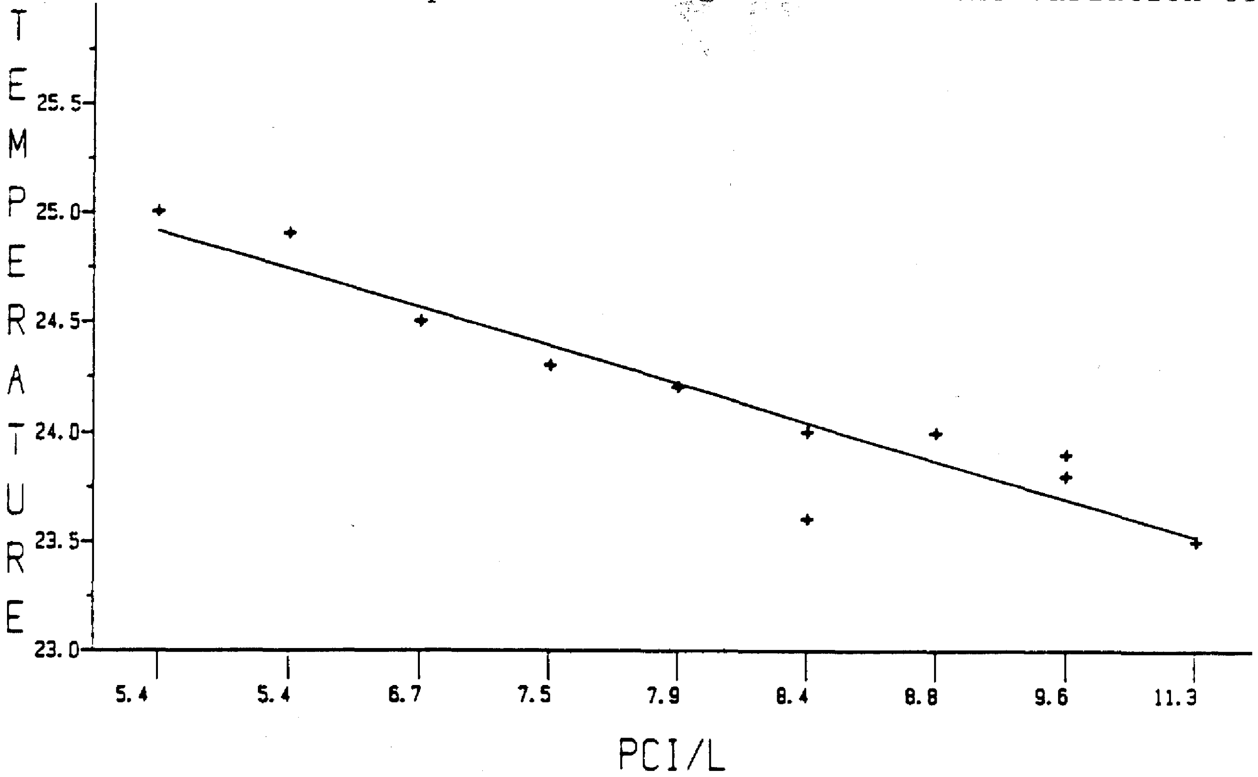

Fig. 2. Variation of Radon Gas Concentration (pCi/l) with Temperature (Degrees Celsius).

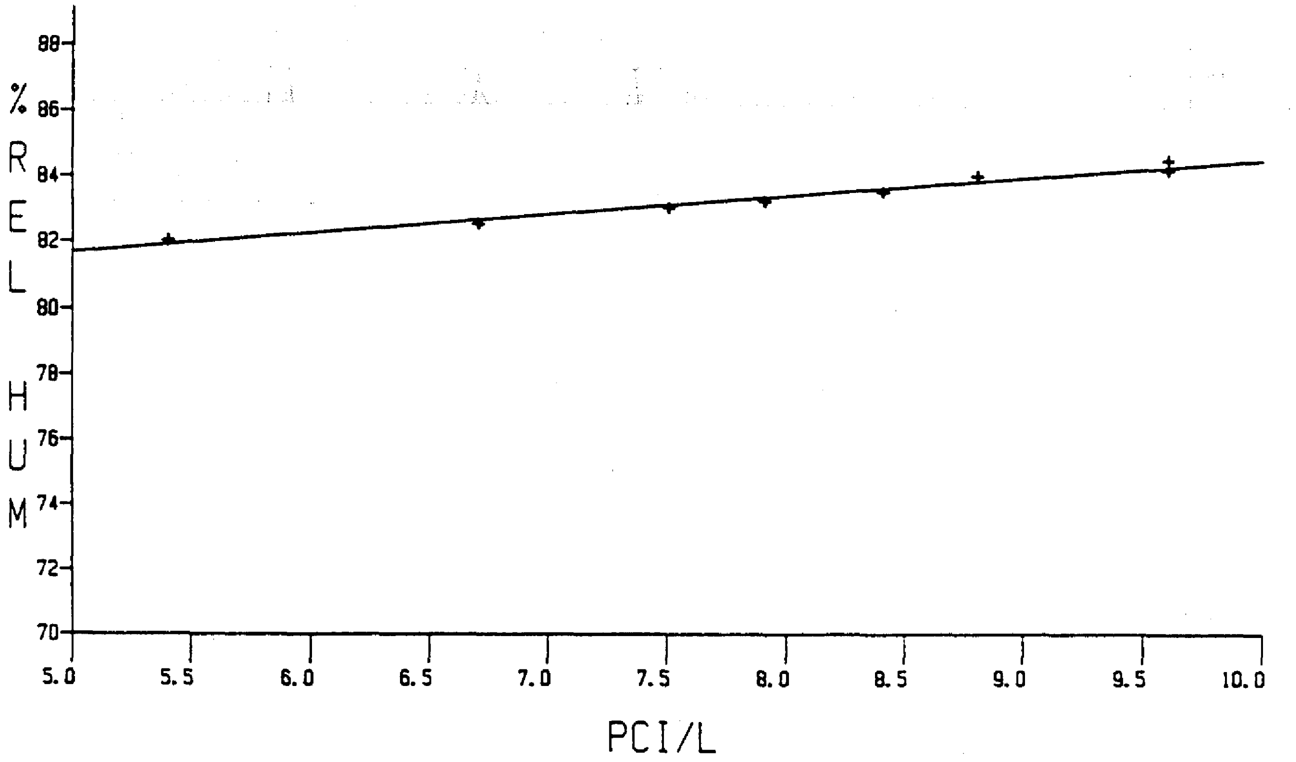

Fig. 3. Variation of Radon Gas Concentration (pCi/l) With Relative Humidity (Percent).

radon levels with temperature and Figure 3 shows the variation with relative humidity. It can be seen that radon gas concentration correlates reasonably well with both temperature (correlation coefficient of -0.80) and relative humidity (correlation coefficient of 0.45). A correlation between radon levels and atmospheric pressure was not possible to determine because of the small pressure changes during the measuring period.

Average values of radon concentration in the test structure were obtained using track etch detectors. These detectors were exposed for periods of one month and returned to the supplier for evaluation. These values are given in Table 1. The radon levels range from 2.9 to 5.6 pCi/l with a mean of 4.06 pCi/l and a median of 3.9 pCi/l. Using a working level ratio (the ratio of radon daughters to radon gas) of 0.5 (Stranden et al., 1979), this results in an average value of 0.02 WL.

TABLE 1: Average Radon Concentrations

Exposure Period	Radon Concentration	
	pCi/l	WL
06/13/84 - 07/12/84	2.55	0.0130
08/07/84 - 09/13/84	2.33	0.0120
09/16/84 - 10/30/84	2.22	0.0110
11/09/84 - 12/11/84	2.14	0.0107
12/11/84 - 01/11/85	1.41	0.0071
01/23/85 - 03/07/85	1.19	0.0060

Table 2 shows the effect of coating the phosphogypsum panels with several kinds of paint and Table 3 gives the composition of the paints.

Table 2: COMPARISON OF RADON SEALANTS

COATING	THICKNESS (mm)	NET COUNT $_{214}$Bi609	FLUX (rel)	C_{Ra} (pCi/l)	$C_{Ra}+C_B$	%RED	AV. WL
BARE		1010	1	3.3	3.8		0.019
1	0.25	25	2.5X10^{-2}	8.3X10^{-2}	0.58	97.5	0.003
2	0.15	150	0.15	0.50	1.0	85.0	0.005
3	0.72	505	0.5	1.55	2.15	50.0	0.011
4	0.40	958	0.95	3.14	3.64	5.15	0.018

Table 3: PAINT COMPOSITION

1. Semi-gloss ALKYD Enamel A40-W5, Sherwin Williams Company	
pigment by weight	42%
Titanium-Dioxide Type III	27%
Calcium Carbonate	14%
Silicates	1%
vehicle by weight	58%
Alkyd resin modified with Linolenic, Linoleic, Oleic and Stearic Acid	24%
Aliphatic Acid	33%
Driers	1%
2. Epoxy Paint	100% Epoxy
3. Filler + Titanium-dioxide + Acrylic Resin, Sherwin Williams Company	
filler + pigment by weight	52%
Titanium-dioxide	13%
Acrylic Resin	20%
Water	15%
4. Interior Flat Latex A27 Wl0, Sherwin Williams Company	
pigment by weight	28%
Titanium-dioxide Type III	19%
Silicates	9%
vehicle by weight	72%
Vinyl/Acrylic/ Polyester Resin	21%
Water	51%

DISCUSSION

Despite large variations in the radon levels in the test structure, the average value was 0.02 WL. This corresponds to the maximum allowable radon level for houses and is a value considered acceptable by the Environmental Protection Agency and the State of Florida. In evaluating these data for the purposes of using phosphogypsum panels in house construction, it must be remembered that the structure in which these values were measured, was totally closed and the panels were painted on the outside. However, since the structure was raised off the ground, if such a house were to be built on grade, the possibility of entry of radon from the soil would have to be considered.

The initial measurements of radon levels in the test structure were encouraging in that the levels were within the maximum allowable. However, it. is clear that if such materials were be used in commercial construction, the radon levels would have to be considerably lowered. Our results, using painted panels of the same type as used in the room, show that radon emanation can be reduced by over 95% when the panels are coated with commercially available paints. We are in the process of remeasuring radon levels in the structure after the walls were painted on the inside. The panel construction is particularly advantageous since the hollow core will provide an avenue for the radon to escape away from the interior of the building when the walls are sealed on the inside.

The use of phosphogypsum bricks for exterior construction appears to open many possibilities for the use of this phosphate by-product. We are in the process of manufacturing several bricks utilizing varying compaction pressures. The radon emanation from uncoated and coated bricks will be measured. We are also concerned that a build up of gamma activity will occur in a brick coated to prevent radon emanation. For this reason, gamma activity will be documented as a function of time.

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REFERENCES

Hartley, J.N. and H.D. Freeman. 1986. Radon Flux Measurement on Gardinier and Royster Phosphogypsum Piles Near Tampa and Mulberry, Florida. EPA Report.

Jonassen, N. 1977. Exhalation of Radon-222 from Phosphate Fertilizers and other Porous Materials. Report, Laboratory of Applied Physics I, Technical University of Denmark.

Medora, R. 1986. Measurement of Radon-222 Levels in a Modular Structure Made from Phosphogypsum and Correlation with Meteorological Parameters. M. Sc. Thesis, Univ. Miami.

Stranden, E., L. Berteig and F. Ugletveit. 1979. A Study on Radon in Dwellings. Health Physics. 36: 413.

THE IMPACT OF A PHOSPHOGYPSUM ROADWAY ON LOCAL GROUNDWATER QUALITY - A CASE STUDY

by

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ABSTRACT

This paper reports on the results of a study that is currently underway to determine the impact of a phosphogypsum roadway on local groundwater quality. The monitoring well array and local hydrogeology are described. The results to date indicate that the local groundwater quality has not significantly changed since the construction of the roadway.

INTRODUCTION

A study has been initiated in rural Polk County, Florida, to determine the effect on local groundwater quality of building a roadway containing significant amounts of phosphogypsum. The chemical constituents of the groundwater have been monitored both before and after construction. This paper reports on the measurement techniques used, the analysis of collected data, and conclusions that may be drawn based on the data collected to date.

SITE DESCRIPTION

The orientation of the monitoring wells relative to the constructed roadway is shown in Figure 1. The section being studied is approximately 600 ft long, and 20 ft wide and is bounded on both sides by ponds of water. The entire area is reclaimed land from phosphate mining activities. Subsurface data obtained during well installation indicate that the region is mildly inhomogeneous with varying depths of sand overlaying clayey sand with phosphate and sandstone fragments. Water levels in the adjacent ponds directly influence the direction of movement of the groundwater. Because of the variability in flow direction, the monitoring wells have been placed symmetrically about the roadway with 6 wells within 30 ft of the centerline and 4 wells within 80 ft of the centerline. The base of all wells have been placed at the same elevation and are approximately 10 ft below the mean. groundwater level. With a screen length of 10 ft, the wells have been designed to measure predominantly the effect on the upper layers of the groundwater.

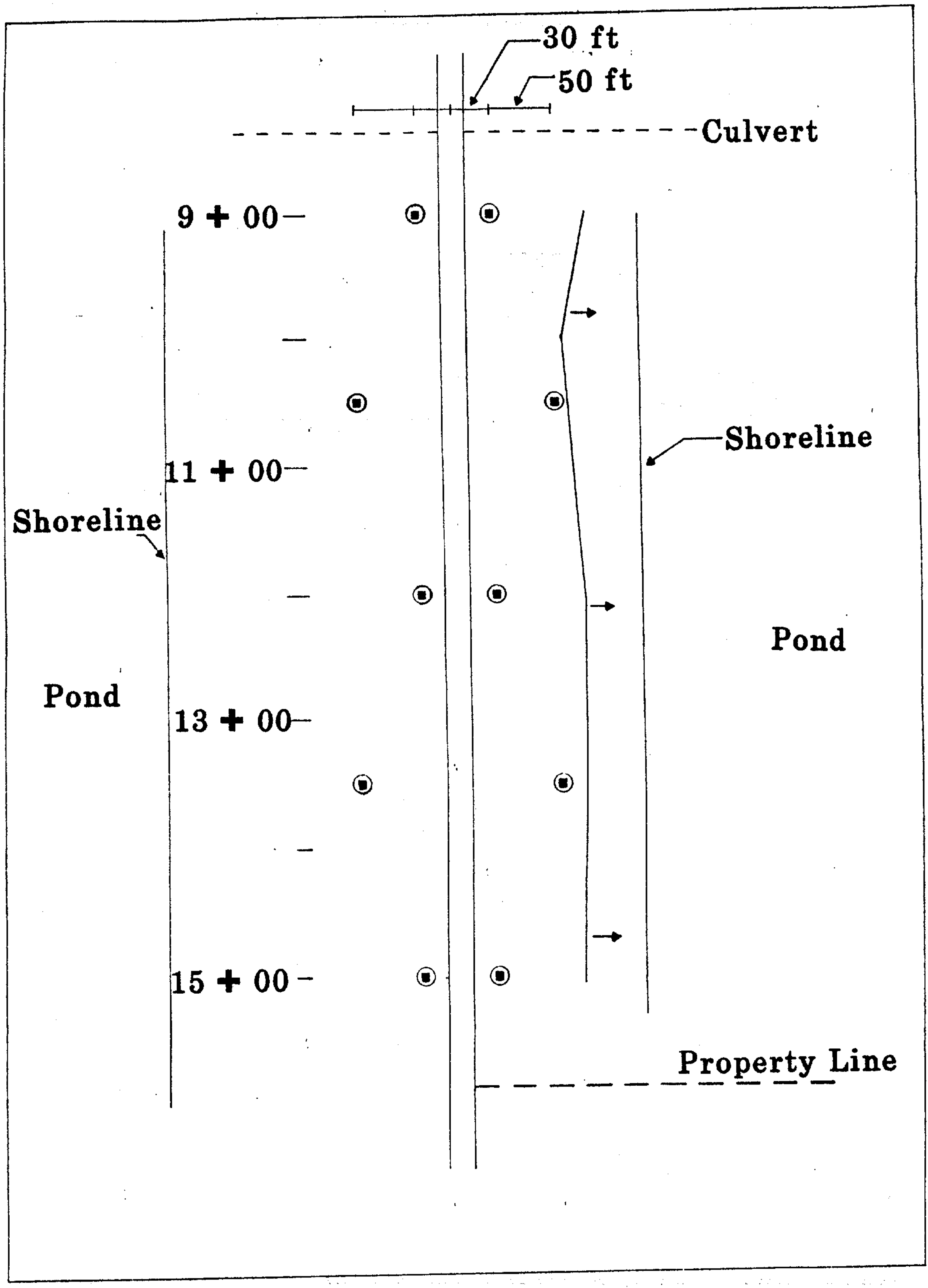

Figure 1. Monitoring Well Locations.

SAMPLING PROTOCOL

The 10 wells adjacent to the roadway are sampled once per month. At each well, the pump is inserted such that the intake is about 9 inches above the bottom of the well. The height of water above the intake varies seasonally between 6 and 11 feet. Since the base of all wells are at the same elevation, the hydraulic conditions are essentially identical in each well. Water is pumped from each well into a four liter beaker where the electrical conductivity is monitored. Sampling guidelines require stability in the electrical conductivity before each sample is collected. Experience with these wells have shown that after pumping approximately three times the volume of water in each well that a stable sample is obtained. At this point the electrical conductivity, temperature, and pH are recorded as well as the color and, odor of the water. At each well, four samples are collected. One is preserved by adding nitric acid to pH less than 2, one by adding sulfuric acid to pH less than 2, a third is simply the raw sample in a one liter polyethylene container, the same type of container used for the acid preserved samples, and a fourth sample is placed in a 300 ml glass container. All samples are refrigerated. The preservation methods correspond to those required by Standard Methods (1985) for the chemical parameters being measured. Samples are then transported to the Environmental Engineering Laboratory at the University of Miami for further analysis. All analyses are done within the time limits specified in Standard Methods (1985).

LABORATORY ANALYSES

For each technique used to measure a chemical parameter, quality control requirements dictate that control samples of known concentration be measured for the chemical parameter and that analysis on every tenth sample be repeated. The precision and accuracy data obtained from these tests are vital for estimating the confidence limits to be associated with the water quality data generated in this study. The results of the quality control program so far are given in Table 1. These data are consistent with, and in most cases better than, that suggested by Standard Methods (1985) and indicate that analytical methods are being performed adequately.

RESULTS

To date there have been eleven sampling trips to the Polk county site. Five of the sampling trips during the pre-construction phase and six have been during the post-construction phase. The dates of these trips are shown in Table 2.

In reporting the results of parameter measurements at the site, it is important to identify the variability that may be associated with the precision and accuracy of the laboratory analyses. A conservative confidence interval of the reported data

Table 1 - Quality Control Data

Parameter	Precision (%)	Accuracy (%)
Fluoride	5.1	6.5
Chloride	1.3	7.5
Ammonium	3.1	16.0
Total Dissolved Solids	5.9	1.4
Alkalinity	0.1	0.4
Dissolved Phosphorous	7.1	5.0
Nitrate	15.0	12.0
Sulfate	8.4	4.0
Sodium	0.2	2.6
Potassium	0.5	2.6
Calcium	0.03	1.9
Magnesium	0.03	3.3
Iron	0.7	1.8
Copper	4.3	7.1
Lead	0	7.1
Chromium	0	6.3
Manganese	0.3	6.3
Cadmium	0	7.7

Table 2 - Sampling Trips

Trip No.	Date	Phase
1	2-21-86	Pre-Construction
2	3-7-86	''
3	3-21-86	''
4	5-15-86	''
5	6-19-86	''
6	10-11-86	Post Construction
7	11-15-86	''
8	12-30-86	''
9	1-31-87	''
10	2-28-87	''
11	3-21-87	''

is the sum of the accuracy and precision errors reported in Table 1. Where appropriate, confidence intervals have been identified where data is reported.

A measure of the overall mineral quality of a water sample is given by the electrical conductivity, total dissolved solids (TDS), and pH. The variability of the site-average values of these parameters is shown in Figures 2 to 4. The electrical conductivity, Fig.2, is seen to remain fairly constant with an average value of 171 millimhos. The TDS, Fig.3, shows a greater degree of variability about a mean value of 142 mg/l. Experimental errors were estimated to be on the order of 7 percent. The results indicate that post-construction TDS levels are lower than pre-construction values by amounts on the order of 10 - 20 mg/l. This change reflects a minor improvement in water quality. The Environmental Protection Agency (EPA) secondary standard for TDS in drinking water is 500 mg/l. The results of pH measurements are shown in Fig.4. The mean value of the measured pH was 5.95. These results show that the site average pH has remained approximately constant for the duration of the study.

Davis and Dewiest (1966) have stated that the major constituents in groundwater, occuring in concentrations of 1.0 to 1000 mg/l, are: Sodium, Calcium, Magnesium, Bicarbonate, Sulfate, Chloride, and Silica. The variability of these parameters, except silica, are shown in Figures 5 to 10, The results of the sodium measurements are shown in Figure 5. The mean concentration is 4.76 mg/l. Experimental errors were on the order of 3%. The results indicate post-construction levels to be slightly less than pre-construction values. The results of calcium measurements are shown in Fig.6. The mean concentration is 38 mg/l. Experimental errors were on the order of 2%. Since phosphogypsum is predominantly calcium sulfate, any significant increase in calcium levels are cause for concern. The results indicate that on Trip No.7 the site-average calcium level rose to 43.5 mg/l, however, on the subsequent trip the level was measured at 38-6 mg/l. This result indicates that this effect was not persistent and probably not due to leaching of the gypsum. The results of magnesium measurements are shown in Fig.7. The mean concentration is 5.52 mg/l. Experimental errors were on the order of 3%. Magnesium levels have not changed significantly since road construction. The alkalinity of the water samples was due solely to the presence of the bicarbonate ion. Alkalinity measurements are shown in Fig.8. The mean alkalinity is 52.4 mg/l. Experimental errors were on the order of 1%. Alkalinity levels seemed to have decreased very slightly, about 2 mg/l, for the last 3 sampling trips. This is not a significant change in this water quality parameter. Sulfate measurements are shown in Fig.9. Because of concerns regarding the quality of data for trips 1 to 4 these measurements had to be rejected. Of the remaining data, the post construction average was found to be 7.48 mg/l. Experimental errors were on the order of 12%. These results show that post-construction levels are less than pre-construction levels. This is significant since phosphogypsum leachate would definitely show up as elevated sulfate levels. The levels found at the site are significantly

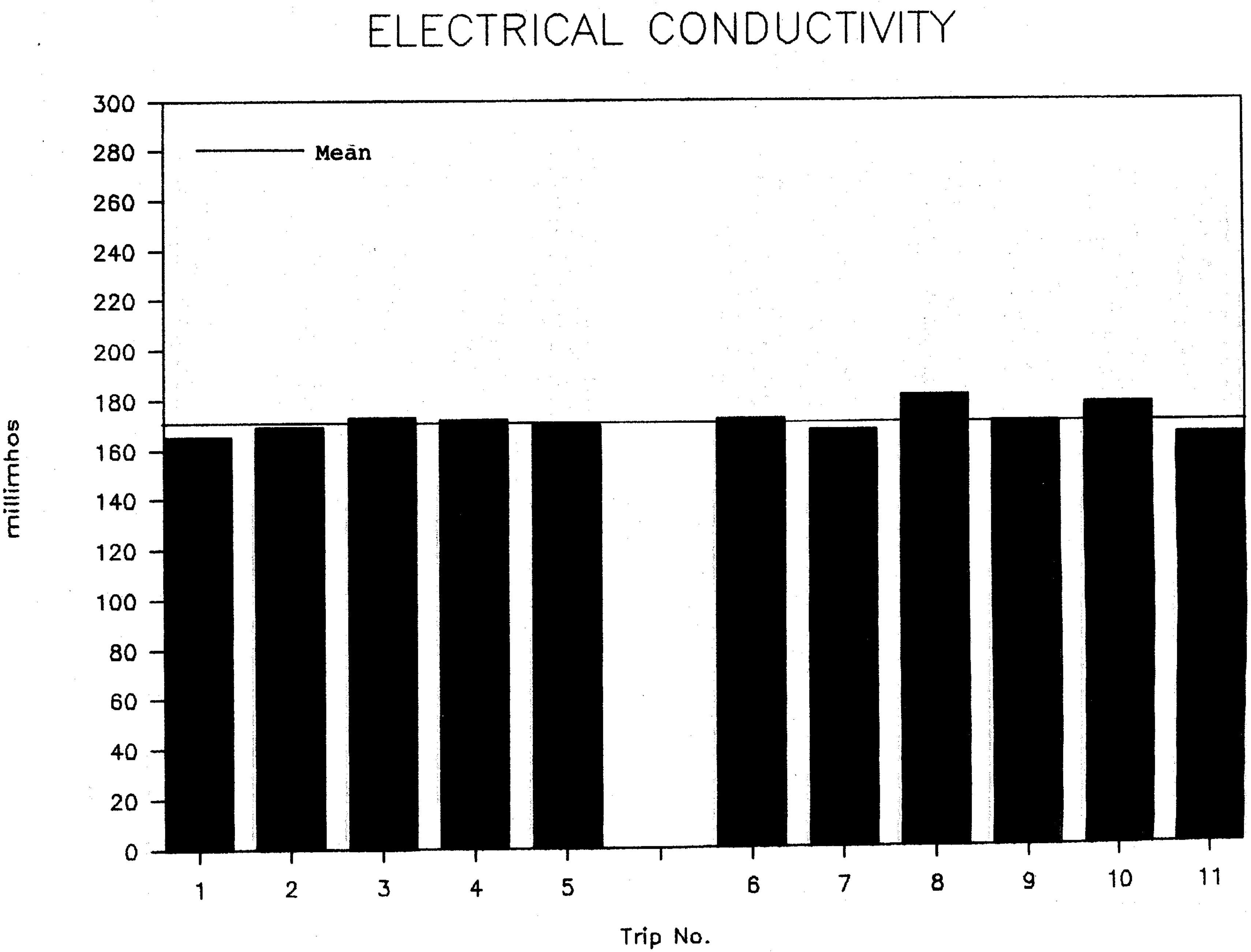

Figure 2. Variability of Electrical Conductivity.

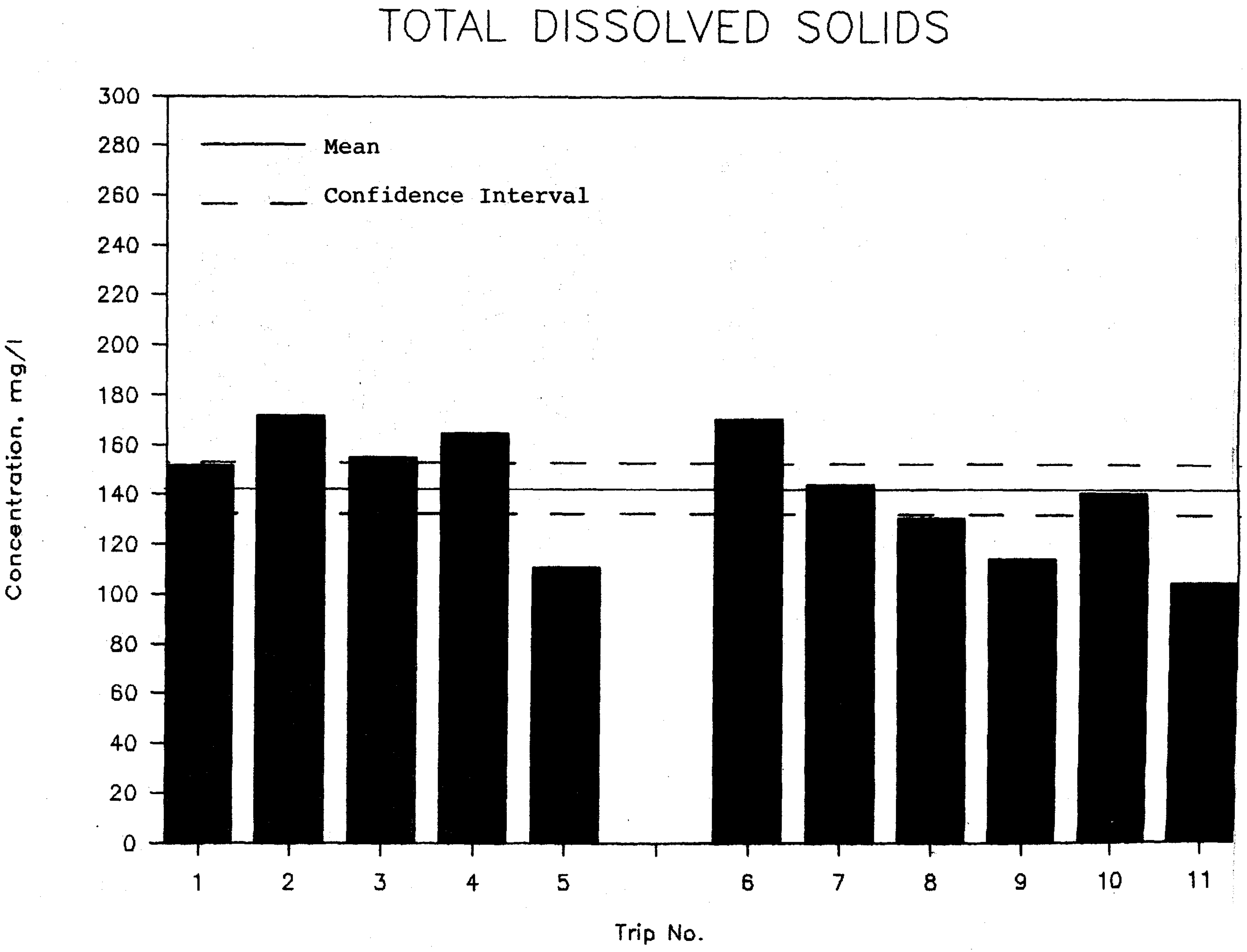

Figure 3. Variability of Total Dissolved Solids.

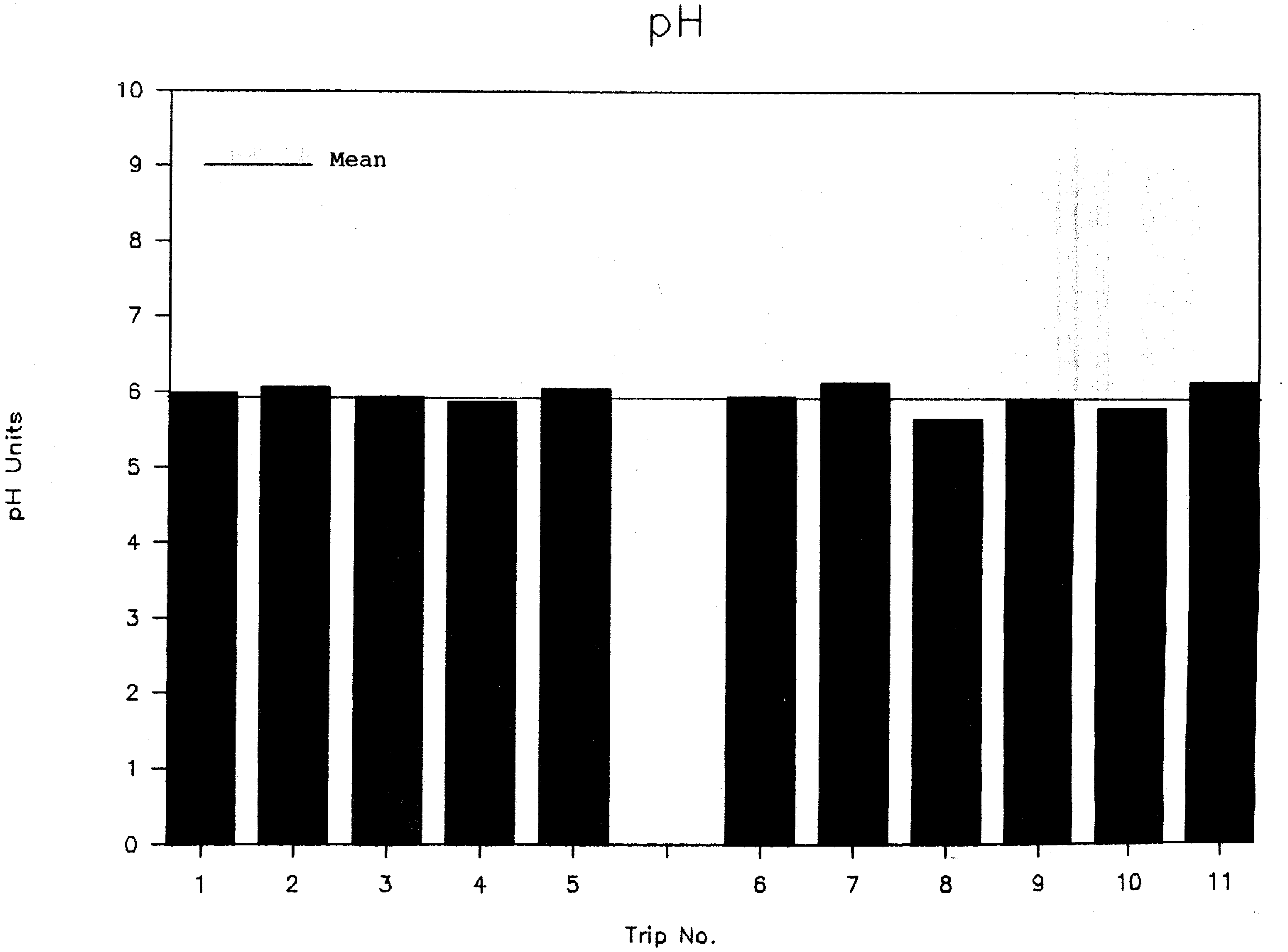

Figure 4. Variability of pH.

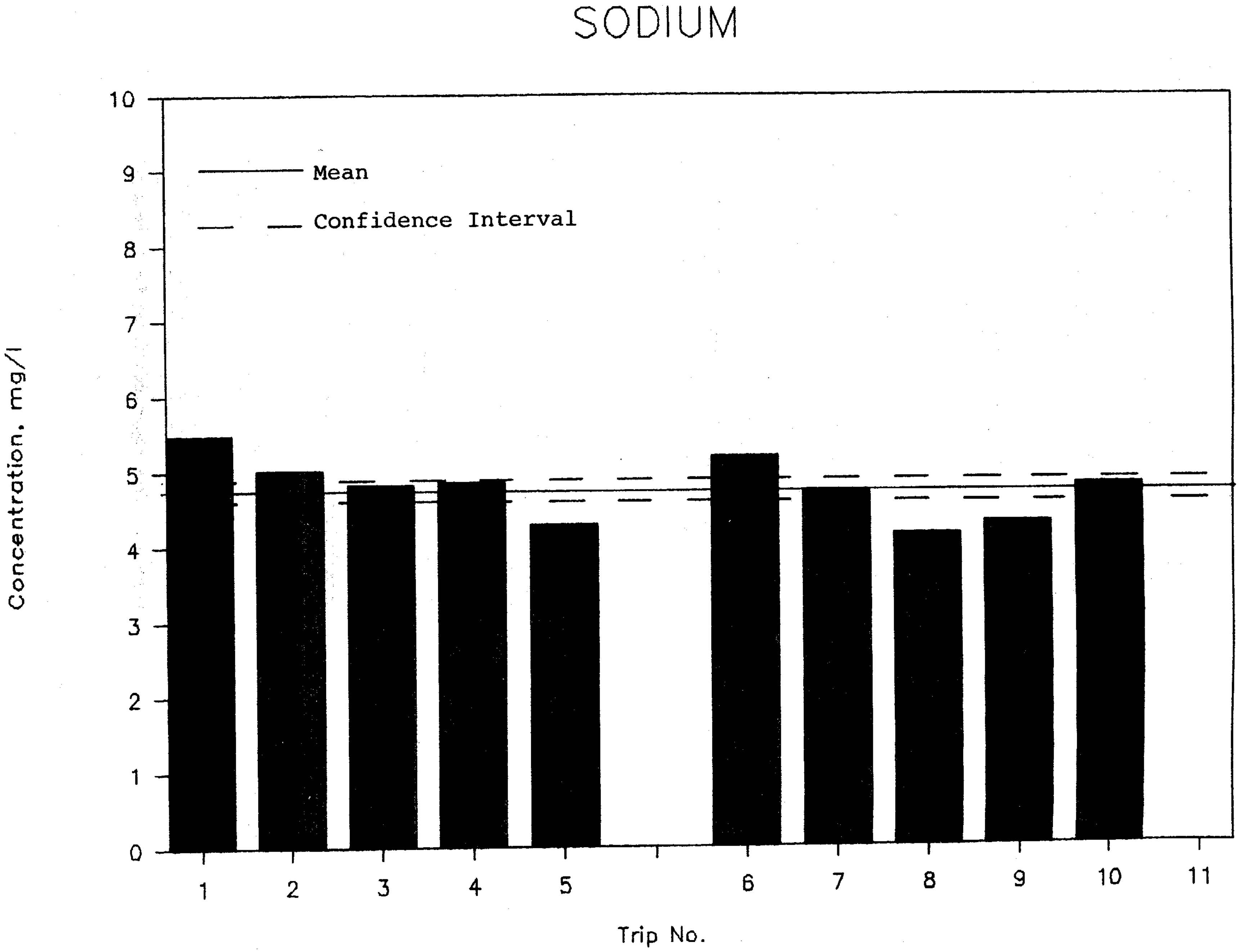

Figure 5. Variability of Sodium.

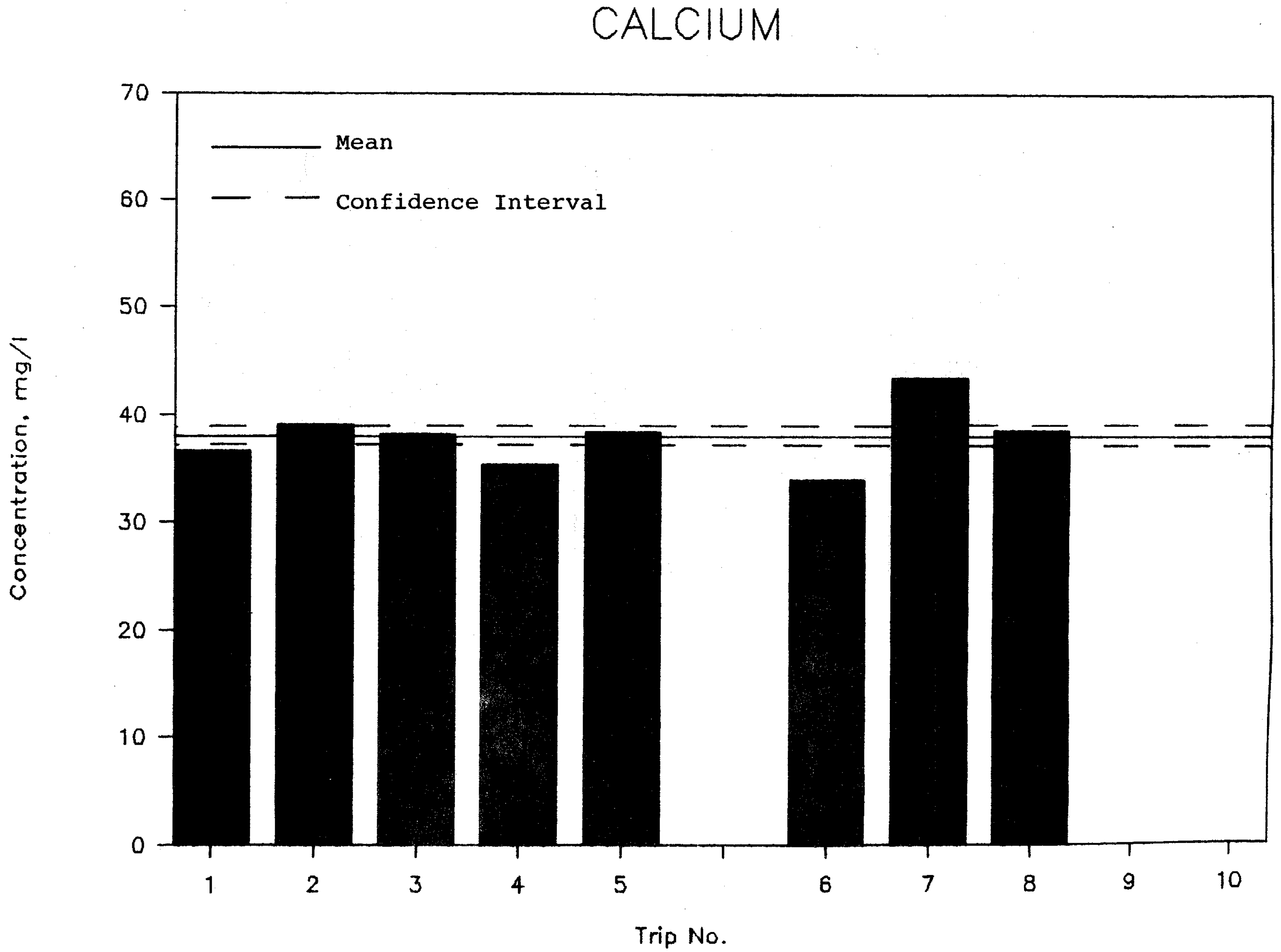

Figure 6. Variability of Calcium.

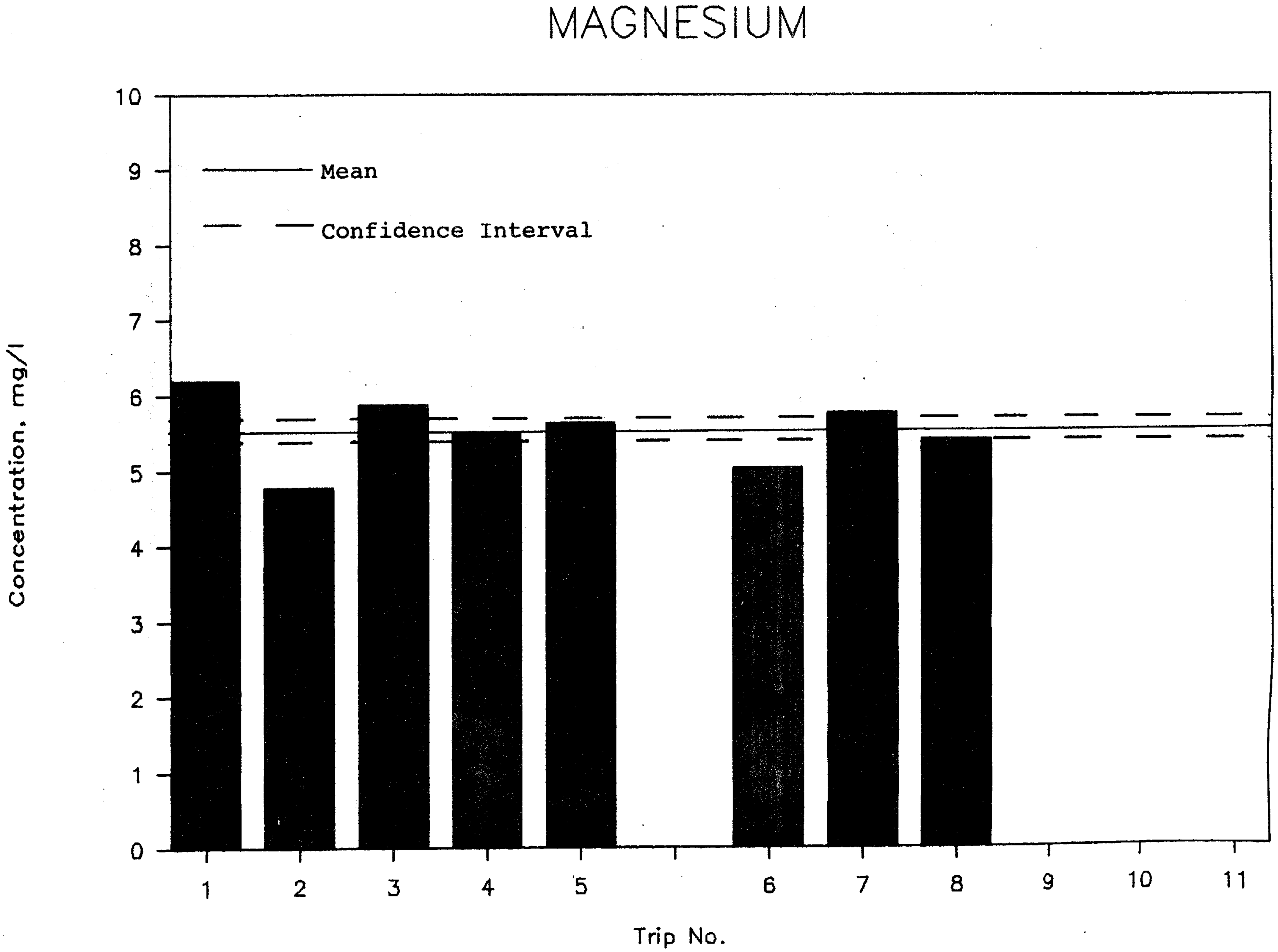

Figure 7. Variability of Magnesium.

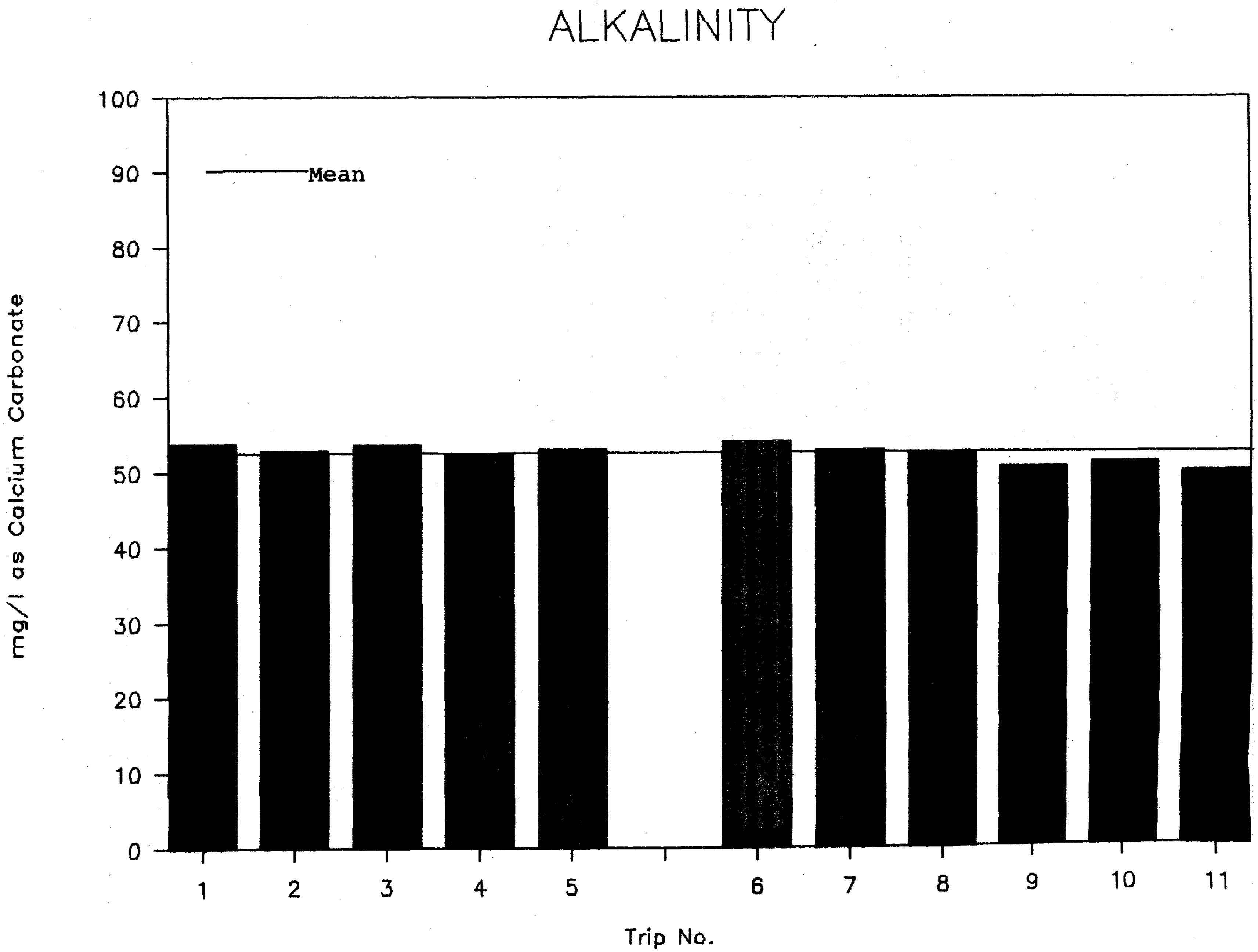

Figure 8. Variability of Alkalinity.

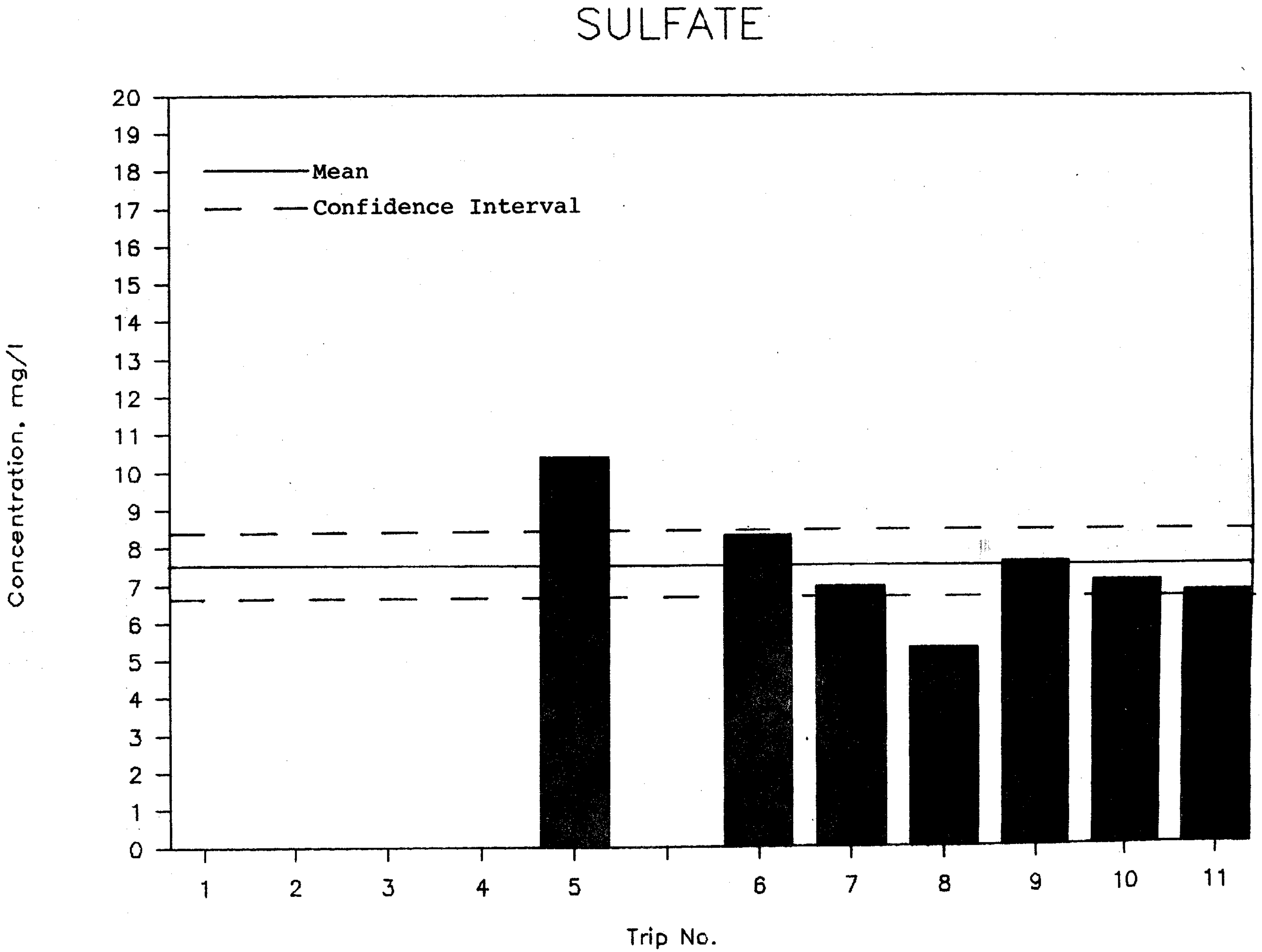

Figure 9. Variability of Sulfate.

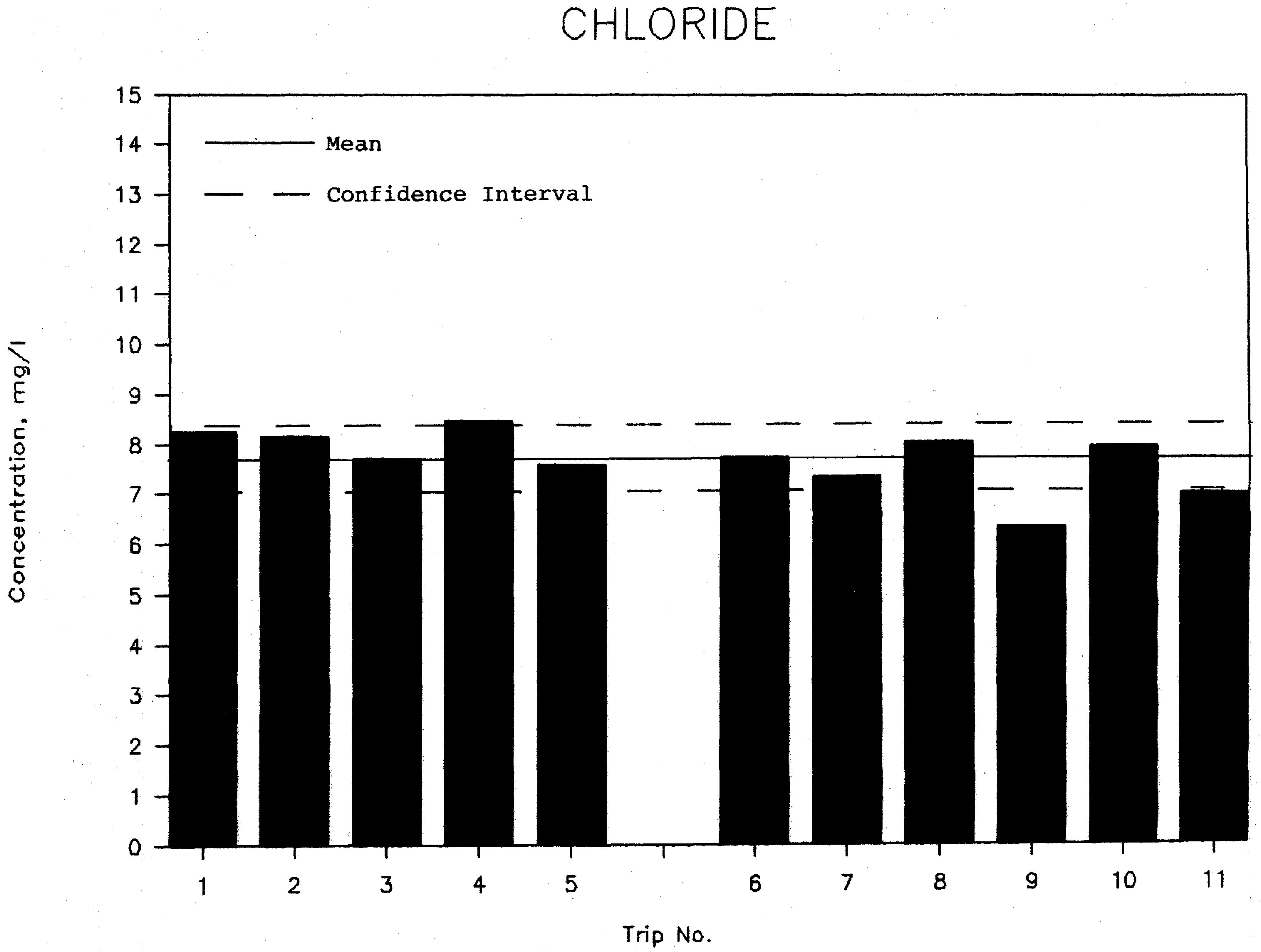

Figure 10. Variability of Chloride

below the EPA secondary drinking water standard of 259 mg/l. Chloride measurements are shown in Fig.l. The mean chloride concentration is 7.69 mg/l. Experimental errors were on the order of 9%. These results show that chloride levels have essentially remained constant so far. The levels at the site are significantly less than the EPA secondary standard for drinking water of 250 mg/l. Although silica measurement was not part of the experimental protocol, one determination of this parameter was done to assess whether silica removal was necessary due to interference in the measurement technique for sulfate. The results indicate that the site average silica concentration is on the order of 6 mg/l.

Secondary constituents in groundwater are (Davis and Dewiest, 1966) Iron, Strontium, Potassium, Carbonate, Nitrate, Fluoride, and Boron. Strontium and Boron were not measured in this study, and carbonate levels were found to be effectively zero for all measurements. The levels of other secondary constituents are shown in Figs.11 to 14. Iron measurements are shown in Fig.11. The mean iron level is 2.51 mg/l. Experimental errors were on the order of 3%. The results indicate that the iron levels measured on post-construction trips 6 and 8 were about 0.4 mg/l above average. Further measurements will indicate whether a trend is being established. Since elevated iron concentrations in groundwater are caused by anaerobic conditions, increased iron levels may be due to a decrease in the oxygen levels in the groundwater. The EPA secondary drinking water standard for iron is 0.3 mg/l. Potassium measurements are shown in Fig.12. These results show that the potassium level in the Trip No.10 sample was about twice the previous average. The significance of this occurance will be evaluated with subsequent measurements. The average of the first 9 samples is 0.53 mg/l. Experimental errors were on the order of 3%. The results indicate that, except for Trip No.l0, post-construction levels are less than pre-construction values, Nitrate measurements are shown in Fig.13. The average nitrate concentration is 1.08 mg/l. Experimental errors were on the order of 27%, indicating the difficulty in measuring this parameter, The results indicate that nitrate levels are fluctuating about their mean value and no significant trend is indicated. The nitrate levels are significantly less than the EPA primary drinking water standard of 10 mg/l. Fluoride levels are shown in Fig.14. The average Fluoride concentration is 0.49 mg/l. Experimental errors were on the order of 12%. The results indicate that the Fluoride levels are effectively constant. These levels remain significantly less than the EPA primary drinking water standard of 1.4 mg/l.

The levels of ammonium, dissolved phosphorous, and other minor constituents such as Copper, Lead, Chromium, Manganese, and Cadmium, are shown in Figures 15 to 17. Ammonium levels are shown in Fig.l5. The average ammonium concentration is l.2 mg/l. Experimental errors were on the order of 19%. The results indicate that pre-construction levels were approximately constant. At Trip No-8, the second trip after construction, the ammonium level suddenly increased and has subsequently returned to the pre-construction level. The reason for this may be seasonal in nature. The phosphorous levels are shown in Fig.l6. The results

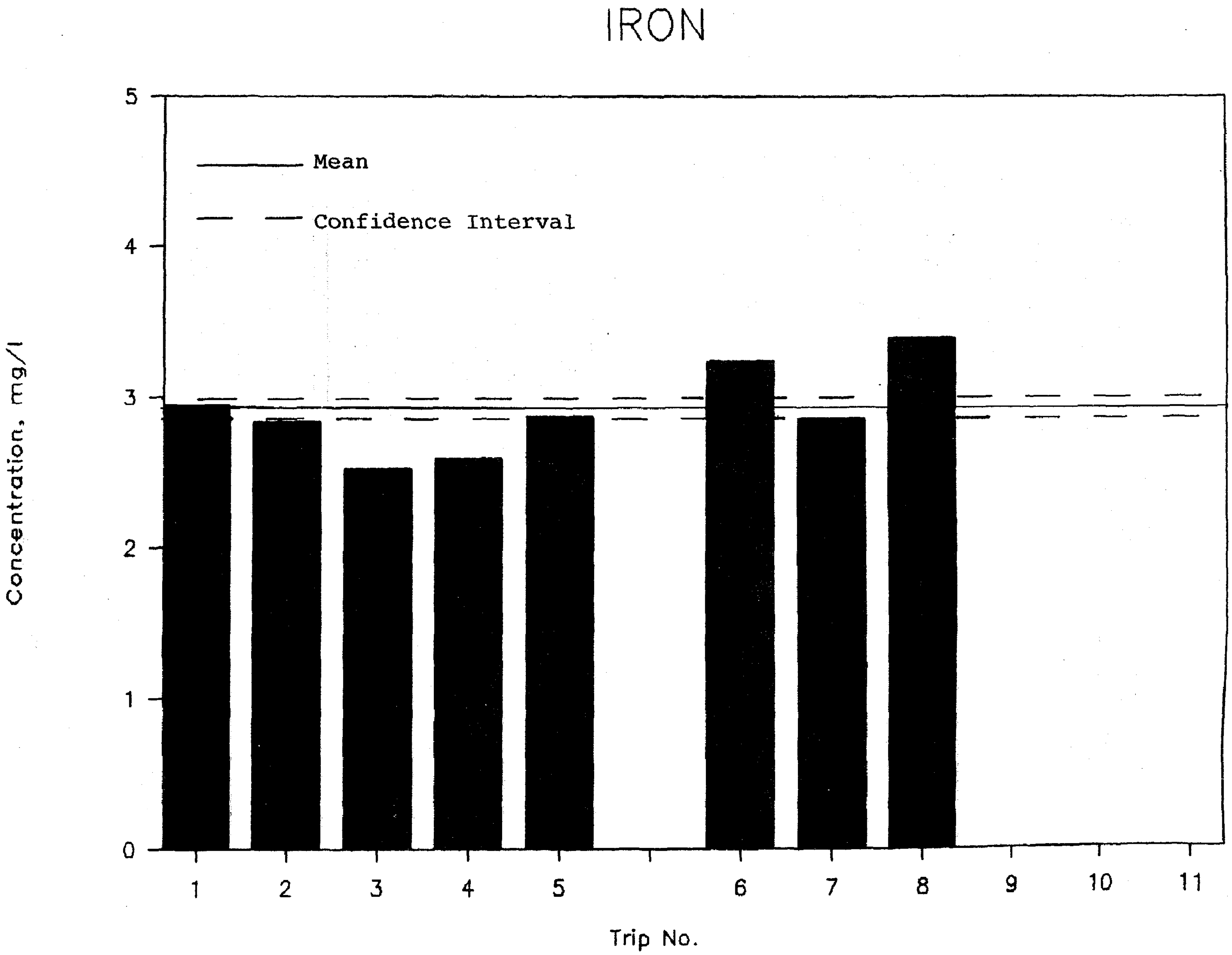

Figure 11. Variability of Iron.

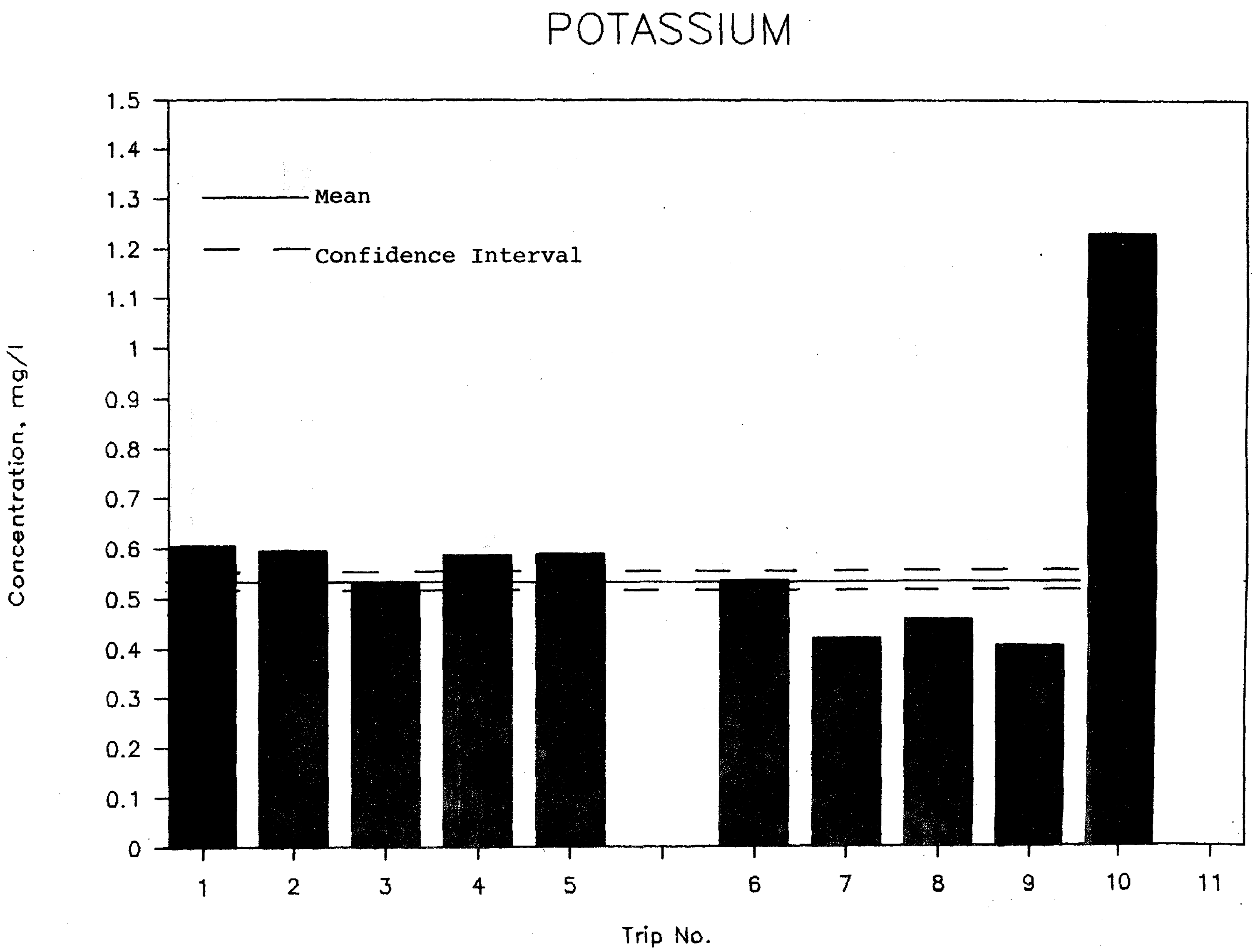

Figure 12. Variability of Potassium.

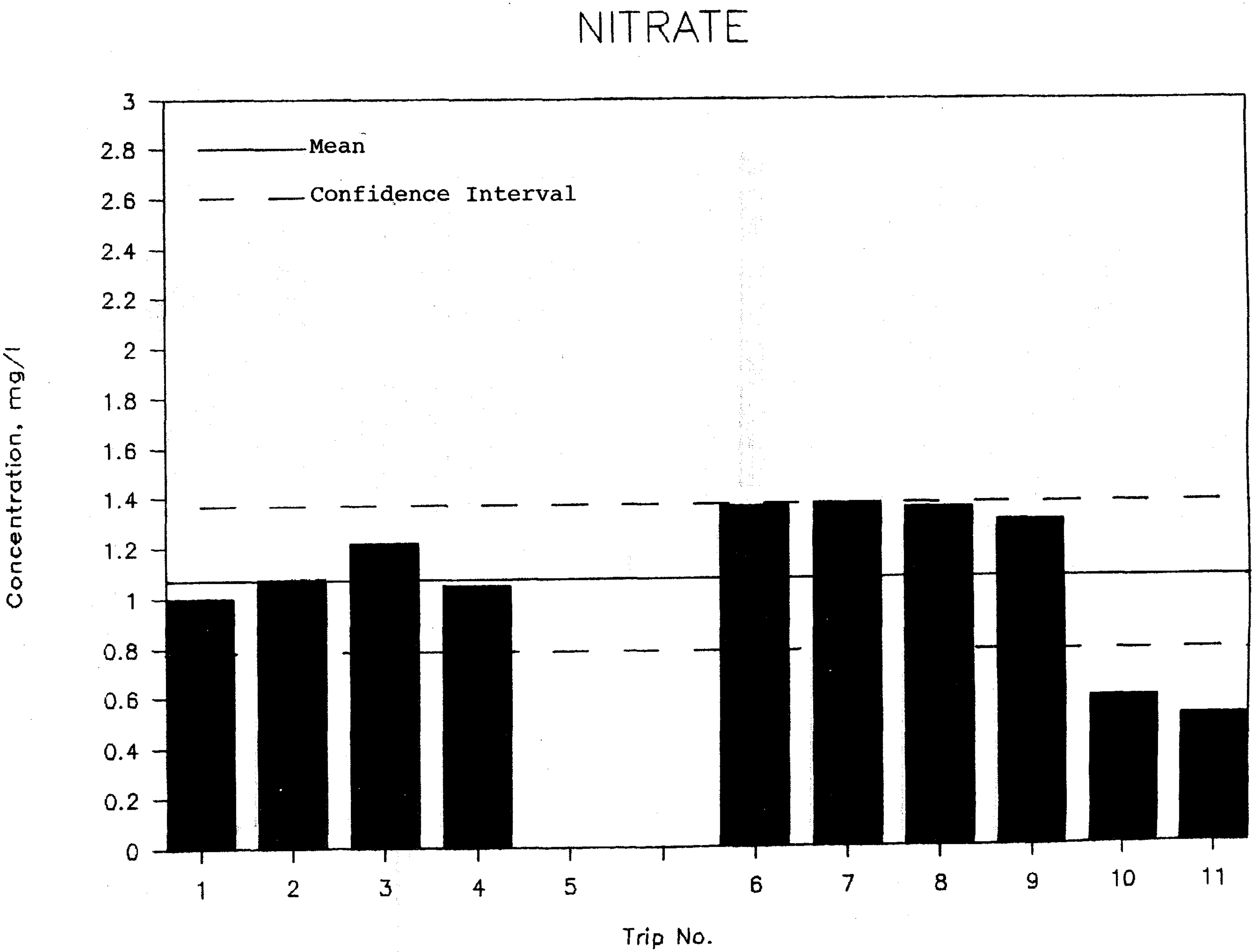

Figure 13. Variability of Nitrate.

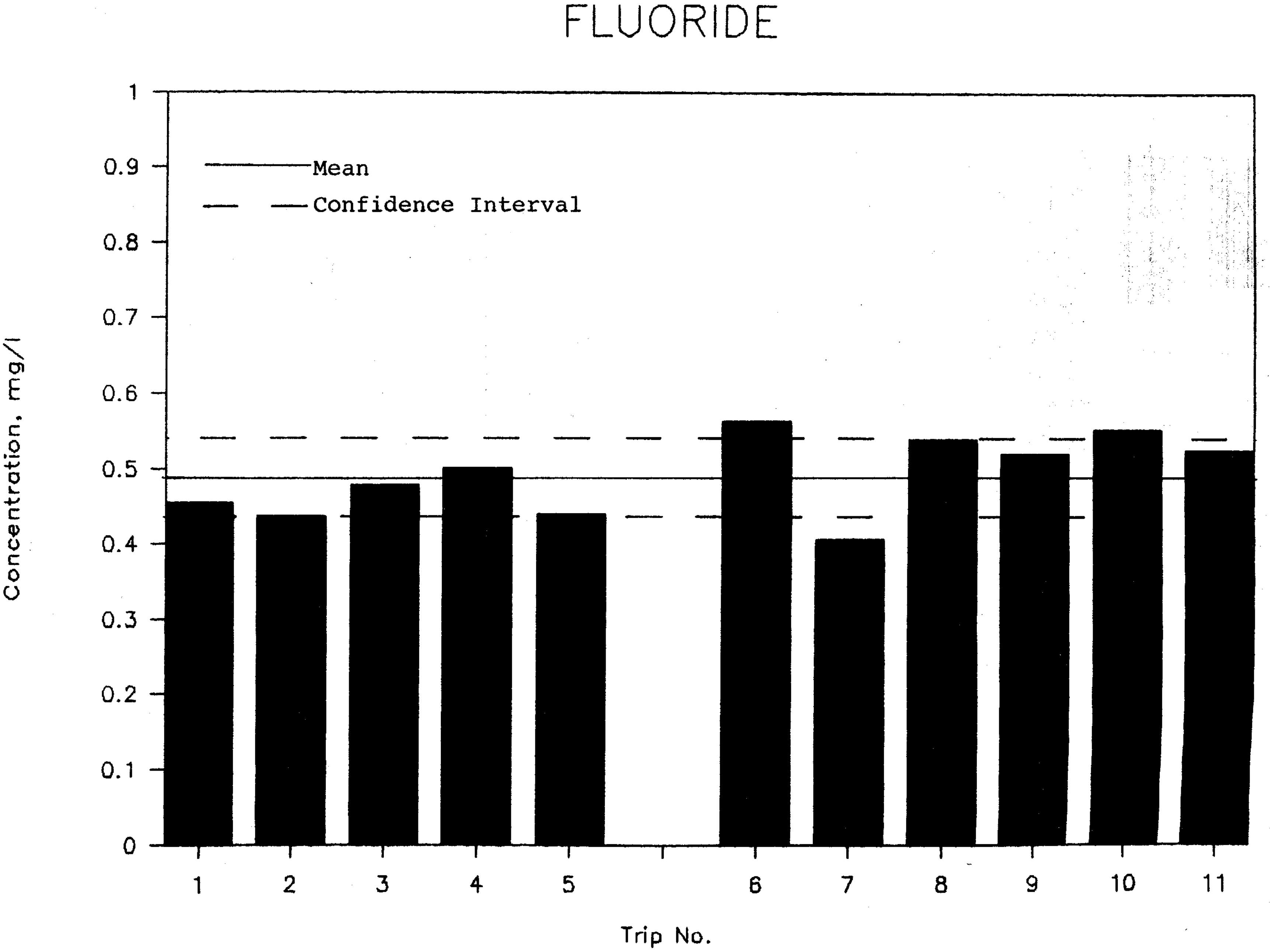

Figure 14. Variability of Fluoride.

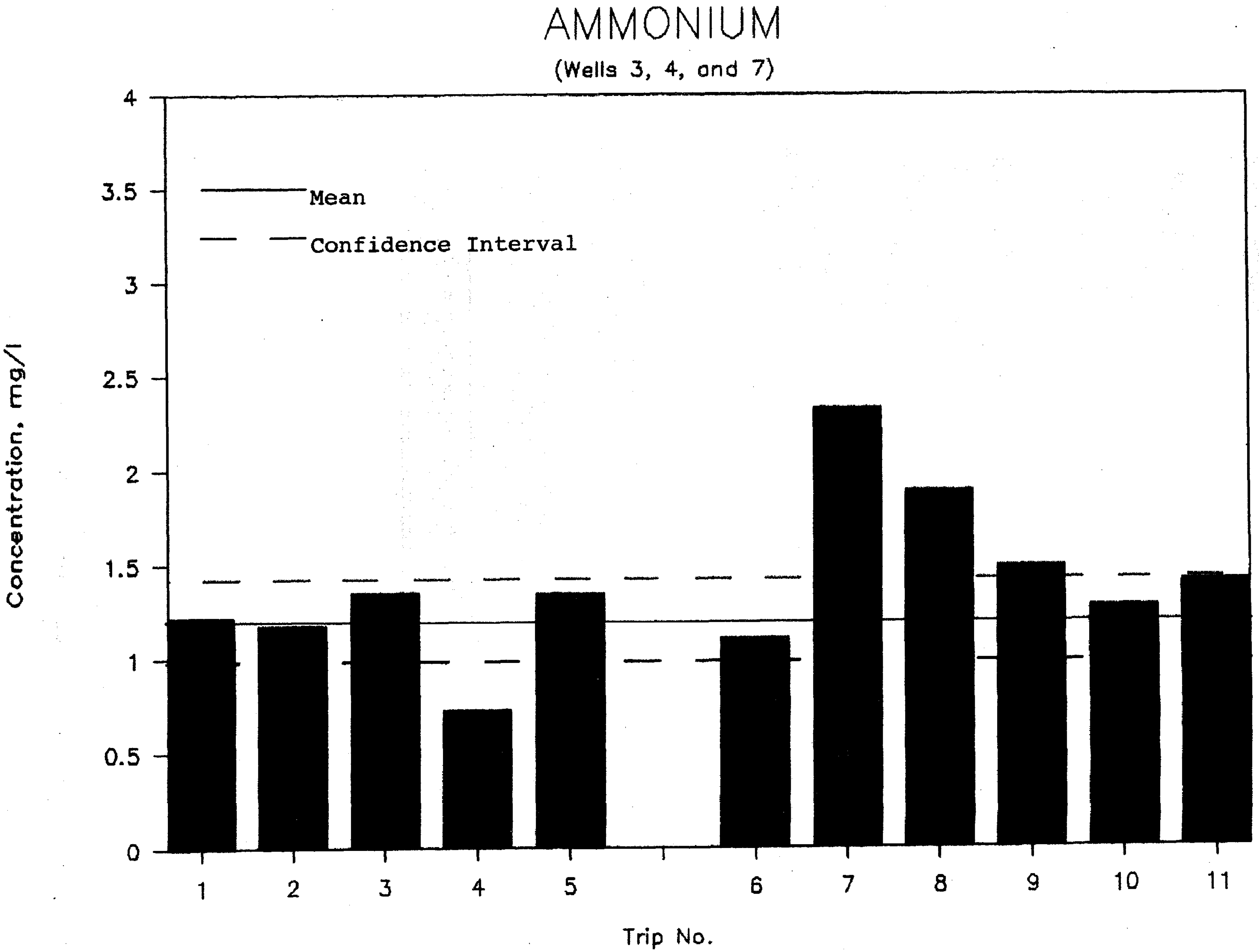

Figure 15. Variability of Ammonium.

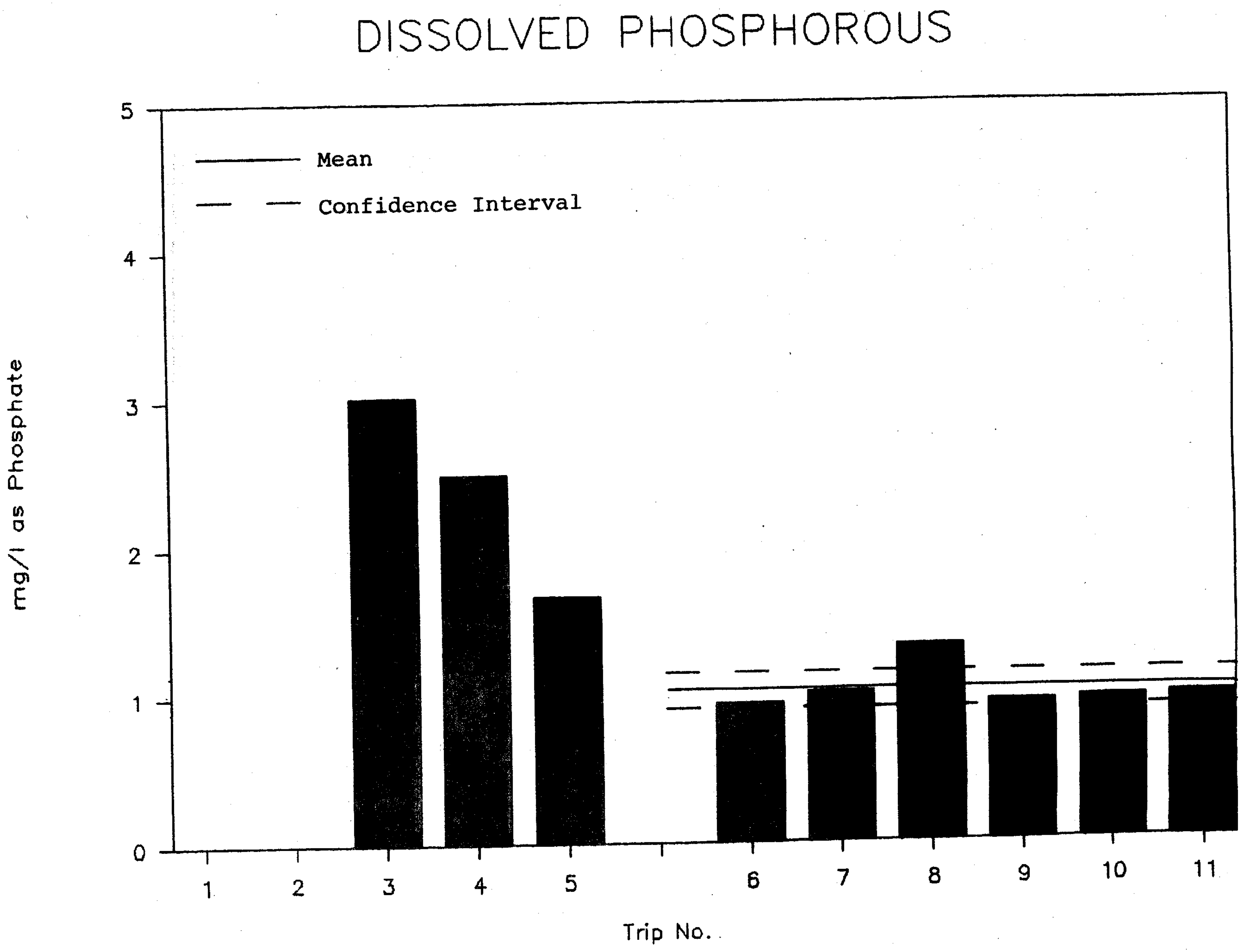

Figure 16. Variability of Phosphorous.

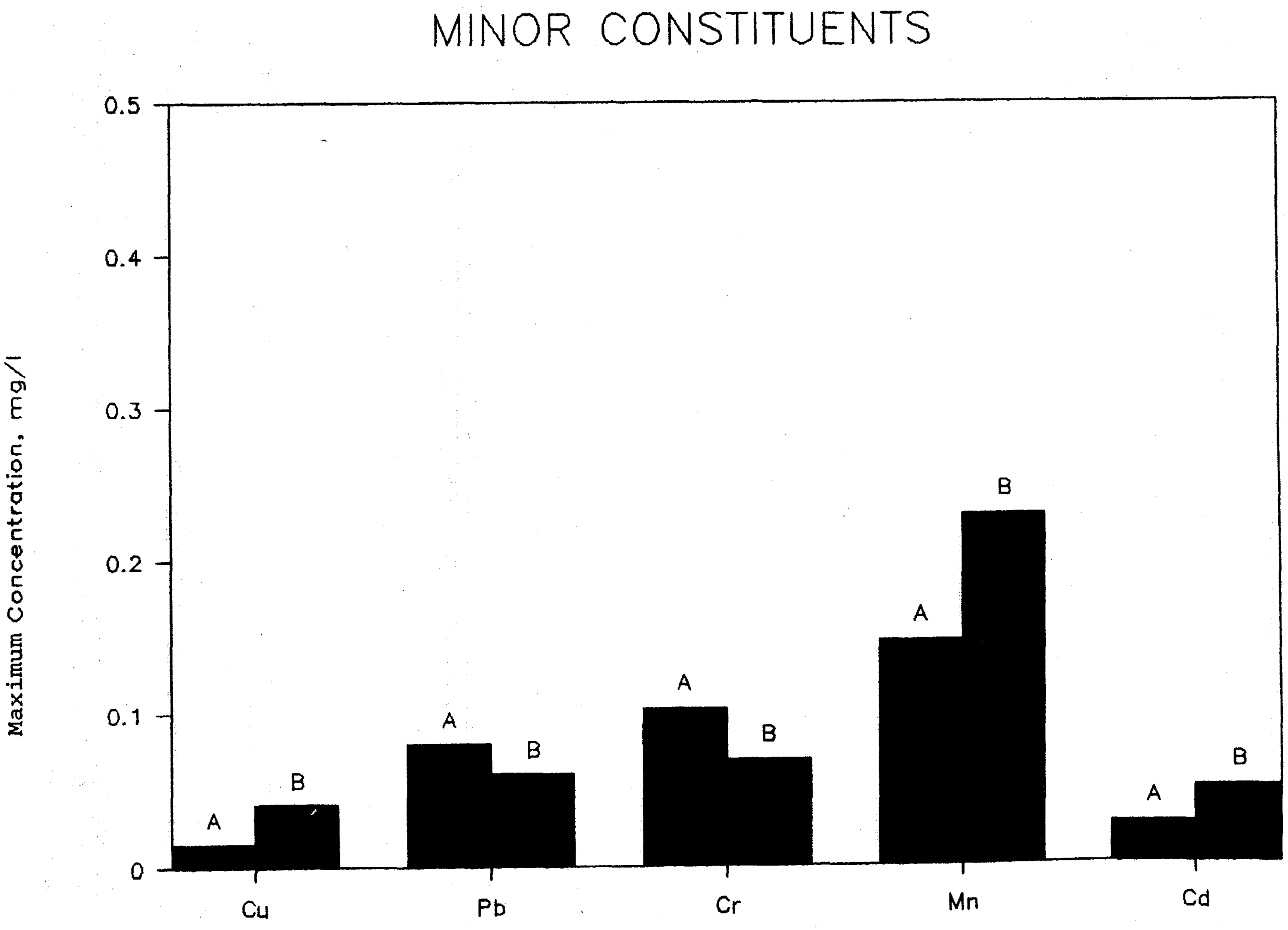

Figure 17. Variability of Minor Constituents

show pre-construction levels to be significantly higher than post construction levels. This may be due to inadequate well development, since there is significant phosphorous levels in the ambient soil. Post-construction levels appear to have stabilized about a mean value of 1.03 mg/l. Experimental errors were on the order of 12%. Figure 17 shows the maximum measured levels of Copper, Lead, Chromium, Manganese, and Cadmium during the pre-construction phase (Phase A) and the post-construction phase (Phase B). There does not not appear to be any dramatic change in the measured levels. In any event, the constituents are not present in significant quanitities in the roadway. A summary of the major water quality parameters is given in Table 3.

DISCUSSION OF RESULTS

It is likely that the impact of the phosphogypsum roadway would be reflected in elevated levels of calcium and sulfate in the groundwater. Both of these parameters have remained either at their pre-construction levels or have decreased since road construction. These results indicate that up to the present time the phosphogypsum has had no measurable influence on the water quality at the site. Because the groundwater level fluctuates between 10 and 15 feet below the base of the roadway and the nearest wells are 15 feet from the edge of the roadway, it is possibly too early to expect any ions to have migrated through the unsaturated and saturated zones to show up in our measurements. Previous studies on the mobility of various parameters in the unsaturated, zone (Todd et al., 1976) have indicated that although sulfate is fairly mobile in the unsaturated zone, gypsum has a significant pricipitation potential. The details of mobility in the unsaturated zone have not been measured in this study, Because of the relatively low pH and high fluoride content of the native groundwater, the acidity and fluoride ions associated with the phosphogypsum are not expected to cause measurable differences in the sampled levels of these parameters.

REFERENCES

Davis, S.N. and R.J.M. DeWeist. 1966. Hydrogeology. John Wiley and Sons, New York,

Standard Methods for The Examination of Water and Wastewater, 16th ed. 1985. American Public Health Association, Washington D.C.

Todd, D.K., R.M. Tinlin, K.D. Schmidt and L.G. Everett. 1976. Monitoring Groundwater Quality: Monitoring Methodology, Report No.EPA-600/4-76-026. U.S. Environmental Protection Agency, Las Vegas.

Table 3 - Summary of Major Water Quality Parameters

Parameter	Level
Electrical Conductivity	171 mmhos
Total Dissolved Solids	142 mg/l
pH	5.95
Sodium	4.8 mg/l
Calcium	38.0 mg/l
Magnesium	5.5 mg/l
Alkalinity	52.4 mg/l
Sulfate	7.5 mg/l
Chloride	7.7 mg/l
Iron	2.9 mg/l
Potassium	0.5 mg/l
Nitrate	1.1 mg/l

APPLICATION OF CHEMICAL EQUILIBRIUM MODELING TO PREDICTION OF THE FATE OF CHEMICAL SPECIES IN PHOSPHOGYPSUM LEACHATE

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ABSTRACT

Transport of chemical components in seepage from phosphogypsum waste is dependent on interactions with the soil or other earthen materials. Competing reactions include complex formation, precipitation, oxidation-reduction, ion adsorption, exchange, and fixation. Computerized models for chemical reactions in aqueous solutions have been adapted for use in soils. One such model, GEOCHEM, was applied as an aid in speciating the chemical constituents of phosphogypsum leachate applied to experimentally simulated soil systems. Results indicated that the model was consistent with experimental observations in some cases, but not in others. The high ionic strength of phosphogypsum solutions, and the lack of thermodynamic constants for mixed solids in the data base, are suggested as reasons for discrepancies between calculated and observed fate of the major chemical components of chemical wastes solutions.

INTRODUCTION

Transport of chemical components in seepage from phosphogypsum waste is dependent on interactions with the soil or other earthen materials. Solute transport models generally include a term for the total solute concentration in the source solution; total concentrations of an element do not, however, provide clues to the chemical form of the element. Such information is essential for estimating the extent to which that element may be adsorbed or transmitted within the soil. Competing reactions in the solution and soil that govern eventual appearance of an element in groundwater are difficult to predict without some application of chemical equilibrium and chemical kinetic principles, particularly when a multitude of chemical constituents are present. Competing reactions include complex formation, precipitation, oxidation-reduction, ion adsorption, exchange, and fixation. Due mainly to oxidation-reduction, ion adsorption, exchange, and fixation. Due mainly to the dearth of kinetic data appropriate to modeling of solute transport and reaction in soils and groundwaters, the more common types of chemical models in existence are based on chemical equilibrium as defined by equilibrium constants. The mass action equations are substituted into the mass balance condition; the resulting set of nonlinear equations is solved simultaneously, usually by an iteration procedure (Nordstrom et al., 1979). This approach is illustrated in Figure 1.

The chemical behavior of ions in solution is governed by the activities of the ions; chemical equilibria are defined by ion activities. In dilute solutions and for practical applications, ion concentrations can often be substituted for activities. Ionic activity is markedly affected by large quantities of other ions in the solution, i.e., by high ionic strengths. Phosphogypsum leachate can have ionic strengths comparable to that of sea water, and in such cases, chemical equilibria calculated on the basis of the analytical concentrations will be in error. Concentration values should be converted to ionic activities by multiplication with an activity coefficient, prior to use in chemical calculations. These coefficients generally range from about 0 to 1, and are calculated from the ionic strength of the solution by one of several semi-empirical equations. An example of the latter is the Davies equation,

$$\log \gamma_i = - Az^2\left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I\right) \qquad (1)$$

where γ_i is the activity coefficient of ion i, A is a constant (approximately 0.5 for water at 25°C), z is the valence of the ion, and I is the ionic strength of the solution. The latter is most easily approximated from measurement of the electrical conductivity (EC) of the solution,

$$I = 1.6 \times 10^{-5} \times EC_{\mu mohs} \qquad (2)$$

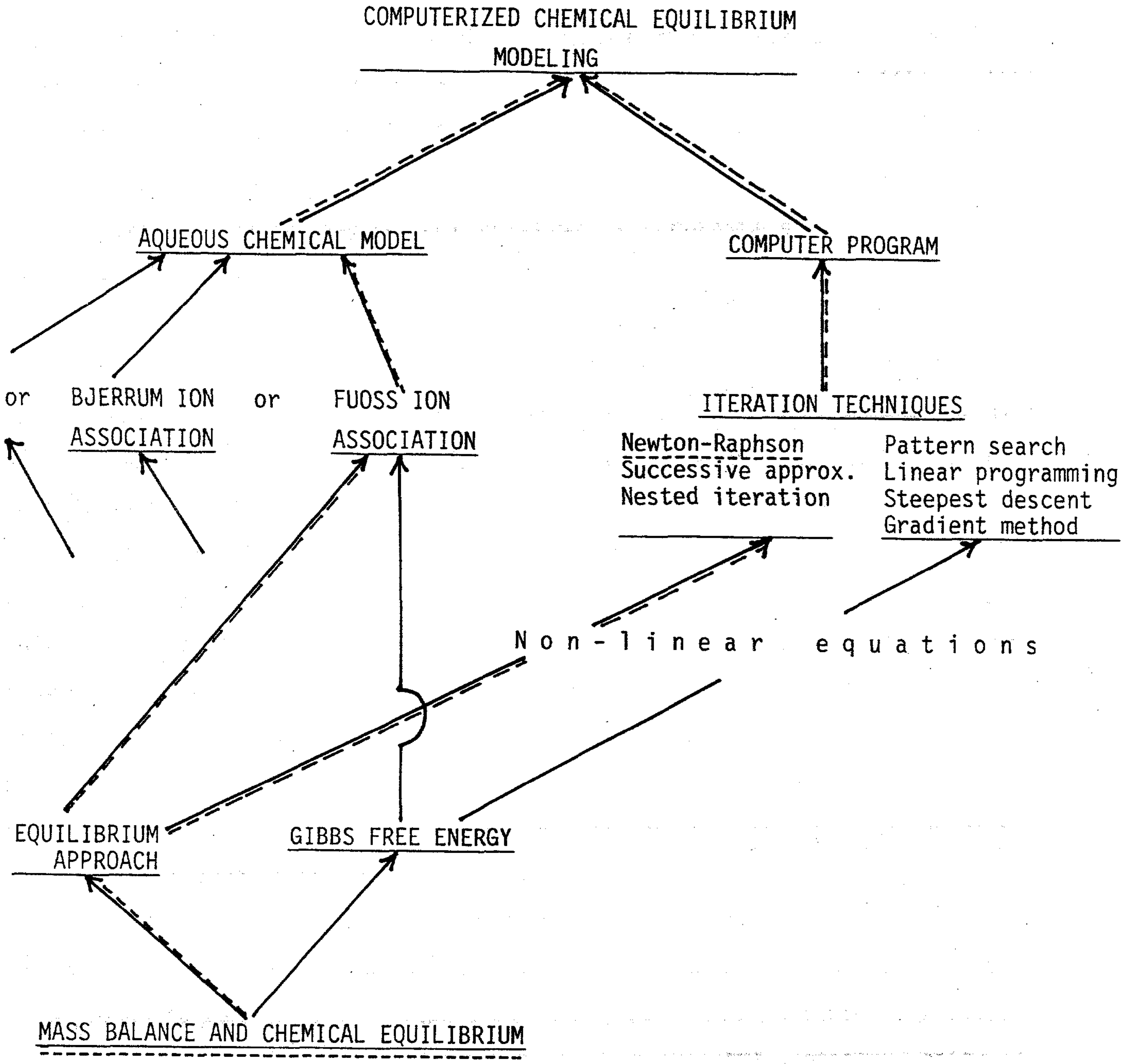

Figure 1. Schematic Diagram of Alternative Approaches to Computerized Chemical Equilibrium Modeling

(------ GEOCHEM approach)

For example, the calcium ion, Ca++, present at a concentration of 1200 mg/liter in a phosphogypsum solution with ionic strength of 0.45 moles per liter, will have an approximate activity coefficient of 0.3, and will tend to "behave" as if there were only 400 mg Ca++ present per liter of solution.

An additional consideration in the use of chemical equilibrium concepts in modeling solute transport in soils is the concept of solute removal from solution by adsorption and/or exchange of ions on solid phases such as clays and sesquioxides. A few computerized chemical equilibrium models include subroutines for ion adsorption and exchange. Due mainly to difficulties with the theory, particularly that of anion adsorption on iron and aluminum oxides and oxyhydroxides, as well as difficulties with the application of the activity concept to reactants and products consisting partly of solid clay particles, these subroutines have not developed to the stage where predictions are consistently reliable. These problems are further complicated when equilibrium models are applied to cases in which the solution is moving through the soil too rapidly for chemical equilibrium to exist locally between the solution and the soil adsorption-exchange phases. It has been shown in laboratory studies that the occurrence of local equilibrium depends on the ratio of the molecular diffusion coefficient to the hydrodynamic dispersion coefficient, i.e., when the ratio is near unity, local equilibrium exists (James and Rubin, 1979). It has also been demonstrated, however, that in some cases where the hydrodynamic dispersion coefficient was much greater than the molecular diffusion coefficient, the local equilibrium assumption appeared to be valid (Valocchi, 1985).

An important concept involved in ion adsorption on soil solid phases is the "zero-point-of-charge". This is defined as the pH of the solution at which a solid phase present in suspension has a zero net electric charge on its surface (pH_{zpc}). The net charge on the surface of a solid governs, in large part, the extent of ion adsorption from solution. In general, at pH values above the pH_{zpc} of a solid, the net surface charge tends to be negative, and the solid will adsorb cations; at pH values below the pH_{zpc}, the net surface charge tends to be positive, and the surface will adsorb anions. Some examples of pH_{zpc} are listed in Table I. Such values should not be taken as definitive; they can be affected by the method of determination, by the presence of impurities in natural solids, and by the composition of the suspending solution.

Table I. Illustrative Values for Zero Point of Charge

Solid	pH_{zpc}
α-Al_2O_3	9.1
α-$Al(OH)_3$	5.0
γ-AlOOH	8.2
CuO	9.5
Fe_3O_4	6.5
α-FeOOH	7.8
γ-Fe_2O_3	6.7
"$Fe(OH)_3$" (amorph.)	8.5
MgO	12.4
δ-MnO_2	2.8
β-MnO_2	7.2
SiO_2	2.0
$ZrSiO_4$	5.0
Feldspars	2-2.4
Kaolinite	4.6
Montmorillonite	2.5
Albite	2.0
Chrysotile	>12.0

(Data from Stumm and Morgan, 1981)

The objective of this paper is to illustrate the use of a computerized chemical equilibrium model, GEOCHEM (Sposito and Mattigod, 1979) as an aid in the interpretation of results from a laboratory study with phosphogypsum leachate (PGL) in physically-simulated soil systems (Murray and Lewis, 1985). The approach used in GEOCHEM is indicated by the broken line path in Figure 1.

Other work utilizing GEOCHEM in our laboratory involved the measurement of Radium-226 distribution between the solution and solid phases of uranium mill wastes. This work has relevance to phosphogypsum waste -- phosphogypsum solids can contain, on the average, 20 pCi Radium per gram (May and Sweeney, 1980). The quantity of radium solubilized will depend, to a large extent, on chemical equilibrium conditions existing between the solid and solution phases of phosphogypsum leachate. In turn, this distribution function varies with the chemical nature of the solid radium compound.

MATERIALS AND METHODS

A bulk sample of phosphogypsum liquid waste (PGL) was obtained from a cooling pond at a phosphate mine in Bartow, Florida. Chemical constituents are listed in Table II.

TABLE II -- Chemical Characteristics of Phosphogypsum Leachate

Characteristic	Experimental Value	Literature Values
pH	1.75 (pH units)	1.0-1.8 (pH units)
Fluoride	8,300 (0.44 M)	3,000-10,000
Orthophosphate-P	5,375 (0.17 M)	6,000-12,000 (as P_2O_5)
Chloride	ND	200
Sulfate	6,250 (0.065 M)	2,000-4,000
Sodium	1,800 (0.078 M)	1,600
Calcium	1,200 (0.03 M)	350-1,200
Magnesium	ND	240
Aluminum	115 (0.0043 M)	100-500
Iron	130 (0.0023 M)	70-300
Manganese	ND	8
Electrical conductivity	30 (mmhos/cm)	Not reported

Values are in milligrams per liter, unless otherwise specified. ND=not determined.

Calculation of charge balance indicates a deficit of cations on the order of 0.53 equivalents per liter; the bulk of the deficit is a result of the fact that at pH 1.75, about 67% of the orthophosphate, and 94% of the fluoride (both weak acids), occur as undissociated H_3PO_4 and HF, respectively (equivalent to a total of 0.52 M).

Data and literature citations are from Murray and Lewis (1985).

The uranium mill waste solutions were saturation extracts of dry waste solids obtained from a mill in Wyoming. pH of the extract was 2.48; chemical constituents included sulfate (8,118 mg/l), and radium-226 (4.1×10^{-8}mg/l). Total acid-soluble radium-226 in the solids was 8×10^{-5}mg/kg. Ionic strength of the extract was 0.44 M.

The PGL was subjected to graded serial batch leaching (method of Houle and Long, 1978) in simulated soil systems containing silica sand, $CaCO_3$, kaolinite, Ca-montmorillonite, and $Fe(OH)_3$ as solid phases (Table III)

TABLE III. Simulated Soil Systems

System	System Composition
S	100% Ottawa silica sand
C	100% $CaCO_3$
K	100% Kaolinite
KI	95% Kaolinite, 5% $Fe(OH)_3$
KC	85% Kaolinite, 15% $CaCO_3$
KCI	80% Kaolinite, 15% $CaCO_3$, 5% $Fe(OH)_3$
M	100% Montmorillonite
MI	95% Montmorillonite, 5% $Fe(OH)_3$
MC	85% Montmorillonite, 15% $CaCO_3$
MCI	80% Montmorillonite, 15% $CaCO_3$, 5% $Fe(OH)_3$

Data are from Murray and Lewis (1985)

Leachates were analyzed for orthophosphate, fluoride, sulfate, and pH. Details of the procedures and results were described previously (Murray and Lewis, 1985). Analytical data were input to GEOCHEM, along with pH and ionic strength (the latter is necessary for calculation of ionic activities in solution).

Analytical data for saturation extracts and acid-soluble concentrations of metals and ligands in the uranium waste solids were input to GEOCHEM for calculation of soluble radium-226, after thermodynamic data for this element was taken from the literature and inserted into the program's data base. The model output was compared to experimental determination of radium-226.

RESULTS AND DISCUSSION

Generally, pH of the system was the controlling factor in removal of fluoride, orthophosphate, and (to a lesser extent) sulfate from PGL solutions by the various soil mineral mixtures.

FLUORIDE

At pH values below its zero-point-of-charge, silica (pH_{zpc} = 2.5) tends to develop positively-charged adsorption sites. Computer calculations indicated that 13.8% of the F in PGL consisted of the complexes HF_2^-, AlF_4^-, and FeF_3^- in the sand system, consistent with the experimentally measured amount of F removed (14%). The balance of F was undissociated HF(pK_a = 3.2), thus less capable of adsorption on charged surfaces. As pH in the soil mineral systems was increased to 3.8 or greater, either by addition of clay minerals or $CaCO_3$, essentially 100% removal of F was obtained. Computer calculations indicated that above pH 3.8, F was removed by formation of $CaF_{2(s)}$. Thus, although one does not necessarily need computer calculations to conclude that most of the F in PGL would be removed by limestone, the calculations allowed quantitative estimation of removal, identification of the various compounds likely involved, and estimation of the critical pH needed for solid formation.

The clay minerals removed 13 to 85% of the F in PGL, the amount removed increasing as pH in the systems increased to 4.2. Removal by kaolinite was explained by development of positive charge on the clay (pH_{zpc} ranges from 4 to 6). Computer calculations indicated that the proportion of free F' and the complex AlF_4^- in the PGL increased from 11.2 to 84.4% as pH increased from 1.7 to 4, consistent with the experimental observations.

$Fe(OH)_{3(s)}$ in the experimental systems was found to be ineffective for F removal. Computer calculations indicated that under conditions of the experiments, 74% of the total iron in the mineral system was reprecipitated as $FeP)_{4(s)}$, thus accounting for the lack of adsorption sites for F^- and AlF_4^- in the system. Extrapolating to field conditions, soils of high iron oxide content may remove little F from PGL (contrary to what one might expect) unless most of the orthophosphate in the PGL is previously removed.

PHOSPHATE

Orthophosphate removal in the experimental systems was consistent with computer calculations for the higher pH values when $CaCO_3$ was added, indicating precipitation of calcium phosphates. Similarly, there was agreement with regard to precipitation of $FePO_{4(s)}$ in high-Fe systems as pH increased to 4.

Soluble phosphate in kaolinitic systems in the absence of $CaCO_3$ was reduced almost five-fold by an increase in pH to about pH 3.5. This result is consistent with increased ionization of H_3PO_4 to $H_2PO_4^-$ (pK_{a_1} = 2.1) while maintaining solution pH below the pH_{zpc} of kaolinite such that the net charge on the clay is positive. Chen et al., (1973) found that adsorption isotherms determined for orthophosphate on kaolinite between pH 2 and pH 12 had maxima about pH 4.

Calculations for the montmorillonite-$Fe(OH)_3$ systems were inconsistent with observations: the model indicated that 82 to 100% of the orthophosphate is precipitated as $FePO_{4(s)}$ at pH values of 2 to 5, while experimental results indicated a more gradual removal of orthophosphate, i.e., about 18% at pH 2.5 to 100% at pH 4.2. Montmorillonite was more effective in removing orthophosphate from PGL than kaolinite, a result contrary to what one might expect at the pH values of the respective systems, i.e., the buffering effect of montmorillonite tended to increase pH above the pH_{zpc} of montmorillonite. Orthophosphate in the low-pH PGL systems tends to occur as the completely protonated form; in the range of pH 4-5, formation of the calcium phosphate complex $CaH_2PO_4^+$ may favor adsorption on the negatively charged montmorillonite.

SULFATE

Removal of sulfate from PGL was less affected by pH, and appeared to be governed more by phosphate precipitation and complex formation such that competition by phosphate for anionic adsorption sites on iron oxide was reduced. In calcareous systems at high pH, precipitation as $CaSO_{4(s)}$ appeared to be the major removal mechanism for sulfate. In non-calcareous systems, computer calculations indicated formation of the neutral complex $CaSO_4^0$ as pH increased above 3.5, consistent with experimental observations of decreased sulfate removal.

RADIUM

Calculations for radium-226 in uranium mill waste solutions were largely inconsistent with experimental results. Computer output indicated that all the radium-226 should remain in solution; experimental results, on the other hand, indicated that most of the radium was in solid form. This illustrates a major inadequacy of the existing thermodynamic data base: poor for some elements, and particularly for mixed solids. In the case of radium in uranium mill wastes, and very likely also for radium in PGL, the formation of the mixed solid $RaCaSO_{4(s)}$ rather than $RaSO_{4(s)}$ may control the solubility of radium. It has been shown that in waters saturated with respect to $BaSO_4$, radium solubility is governed by $RaBaSO_{4(s)}$ (Langmuir and Melchior, 1985). Until thermodynamic data are available for mixed solids such as $RaCaSO_{4(s)}$ and $RaCaSO_{3(s)}$, computer modeling of chemical equilibria in waste solutions can not substitute for laboratory or field data, except where large uncertainties in the results are acceptable.

CONCLUSION AND RECOMMENDATIONS

Transport in soil of chemical solutes in phosphogypsum liquid wastes and leachates is dependent on the ionic forms (chemical species) of the solutes, and on ionic activities. Due to the multitude of chemical species in these leachates, and the competing reactions that take place in solutions and in soil, it is impractical to measure all of these with the aim of predicting eventual concentrations in groundwater. The use of computerized chemical equilibrium models can greatly reduce the amount of analytical data needed for prediction, and can enhance predictive capabilities. Such use can not, however, completely eliminate the need for actual measurement.

Difficulties in speciating the chemical composition of phosphogypsum leachate here appeared to arise primarily from:

(a) the high ionic strength of the waste liquid, such that semi-empirical equations developed for aqueous solutions may have been inadequate for correct calculation of ionic activities from concentration values;

(b) the lack of thermodynamic constants in the computer data base, especially those for mixed solids. Also, most of the thermodynamic data in the literature were measured on pure solid phases, and the presence of impurities under field conditions may affect the actual extent of a particular chemical reaction.

On the other hand, use of computerized equilibrium modeling provided reasonably quantitative explanations for a number of phenomena observed that would not have been predicted. Industrial application of such modeling will also:

(a) allow correct selection of chemical species that may require monitoring, and thus greatly reduce the time and cost of monitoring;

(b) provide quantitative guidance for leachate treatment modes for removal of the bulk of chemical contaminants from leachates.

ACKNOWLEDGEMENTS

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REFERENCES

Chen, Y.S.R., J.N. Butler, and W. Stumm. 1973. Adsorption of phosphate on aluminum and kaolinite from dilute aqueous solutions. J. Colloid Interface Sci. 43:421-436.

Houle, M.J., and D.E. Long. 1978. Accelerated testing of waste leachability and contaminant removal in soils. In Land Disposal of Wastes, Proc. 4th Annual Research Symp., U.S. EPA, 600/9-78-016.

James, R. V. and J. Rubin. 1979. Applicability of the local equilibrium assumption to transport through soils of solutes affected by ion exchange. In Chemical Modeling in Aqueous Systems, E.A. Jenne, ed; ACS Symp. Ser 93:225-236. American Chemical Society.

Langmuir, D. and D. Melchior. 1985. The geochemistry of Ca, Sr, Ba and Ra sulfates in some deep brines from the Palo Duro Basin, Texas. Geochim. Cosmochim. Acta 49:2423-2432.

May, A. and J.W. Sweeney. 1980. Assessment of environmental impacts associated with phosphogypsum in Florida. In Phosphogypsum. Proc. International Symposium on Phosphogypsum, D.P. Barris and P.W. Boody, eds. The Florida Institute of Phosphate Research.

Murray, L.C., Jr., and B.G. Lewis. 1985. Phosphogypsum waste anion removal by soil minerals. J. Environ. Engineering (ASCE) 111:681-698.

Nordstrom, D.K. et al. 1979. A comparison of computerized chemical models for equilibrium calculations in aqueous systems. In Chemical Modeling in Aqueous Systems, E.A. Jenne, ed. ACS Symp. Ser. 93, American Chemical Society, Washington, D.C.

Sposito, G. and S.V. Mattigod. 1979 GEOCHEM: A computer program for the calculation of chemical equilibria in soil solutions and other natural water systems. Dept. of Soil and Environmental Sciences, University of California, Riverside.

Stumm, W. and J.J. Morgan. 1981. Aquatic Chemistry. John Wiley and Sons, New York.

Valocchi, A.J. 1985. Validity of the local equilibrium assumption for modeling sorbing solute transport through homogeneous soil. Water Resources Res. 21:808.820.

RUNOFF OF CONTAMINATION FROM PHOSPHOGYPSUM STACKS

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ABSTRACT

The subject of the paper is defining the amount of contamination in surface runoff from phosphogypsum stacks.

The paper aims at presenting the amount of loads characteristic contamination indicators in runoff from dry phosphogypsum stacks.

Investigations concentrate on the problem of phosphogypsum effect on water environment. Researches were carried out for the Chemical Plant "Police" in Poland.

Present research can be used for qualification the degree of contamination of surface water environment resulting from dry phosphogypsum stack runoff.

LIST OF SYMBOLS

D_i - diffusion coefficient in i-direction $[L^2T^{-1}]$,
F - projection area of stack $[L^2]$,
$f_1/t_1/$ - infiltration rate after transformation of coordinate system $/t, f/$ $[LT^{-1}]$,
f_c - infiltration rate for saturated stack $[LT^{-1}]$,
f_o - initial infiltration rate $[LT^{-1}]$,
k - coefficient $[T^{-1}]$,
$L/t_1/$ - load of suspension $[MT^{-1}]$,
$M/t_1/$ - total mass of suspension $[M]$,
n - initial porosity of the stack $[\%]$,
P - parameter of the stack $[\%]$,
q - rainfall rate $[LT^{-1}]$,
q_c - maximum value of the surface runoff rate $[LT^{-1}]$,
$q_s/t_1/$ - surface runoff rate $[LT^{-1}]$,
$S/t_1/$ - concentration of suspension $[ML^{-3}]$,
t - rainfall time $[T]$,
t_o - initial time of surface runoff $[T]$,
t_1 - surface runoff time $t_1 = t - t_o$ $[T]$,
$V_s/t_1/$ - volume of runoff from the stack $[L^3]$,
W - natural moisture of the stack as a water mass to grains mass at $t = 0$ $[\%]$,
β - stack surface slope $[\%]$,

Θ - volumetric water content dimensionless ,

ψ - runoff coefficient dimensionless .

INTRODUCTION

One of the products of the Chemical Plant "Police" is phosphoric acid and phosphogypsum is its by - product. Phosphogypsum stacks amount to 29,6 million tons /up to 1986/, they cover the area of 100 ha /250 acres/. Further development of "Police" plant will result in 0,72 million tons of phosphogypsum per year. At present only about 0,05 % is being utilized annually. Phosphogypsum is transported to the stacks by belt - conveyor.

The plant is situated to the north of Szczecin about 45 km from the Baltic Sea.

Researches include analytical and experimental investigations as well as laboratory model experiments and field work.

ANALYTICAL DESCRIPTION

Presented equations regard the runoff of insoluble pollutants from phosphogypsum stacks. Investigations are limited to definite suspension contamination; therefore the results of experiments presented in the paper can be used for different kinds of industrial stacks which have physical - mechanical features, namely grain - size and specific gravity, similar to phosphogypsum.

In the analytical research the following model of runoff process was assumed: the eroded area is a sort of film /F/ with finite dimensions and given slope / β /. The surface runoff process begins when the rate of rainfall is higher than the infiltration rate. The infiltration rate depends on rainfall rate /q/ and ground surface such as: natural moisture /W/, slope of the surface / β / and parameter /P/ /Rydzyński, 1981/ which includes porosity /n/ and natural moisture /W/ at the upper layer of the ground, Eq . /1/ :

$$P = [\, n - W /1 - n/ \,] \cdot 100 \% , \qquad /1/$$

In Eq . /1/ n and W are dimensionless, and natural moisture /W/ is assumed as a quotient mass of free water in unit volume of ground to mass of ground solid state.

For the further analysis following main simplifications of physical and mathematical model were assumed /Rydzyński , 1986/:

- q /t, F/ = const.,
- β /t, F/ = const.,

- the influence of evaporation was neglected,
- the quantities of the runoff rate and load of suspension coming from any of unit area are constant.

Equations relating to the rate and volume of surface runoff were formulated on the base of mathematical model of infiltration /Rydzyński, 1984/. The initial equation of liquid diffusion was taken as a base for approximation of infiltration rate /Eagleson, 1970/, in the form:

$$\frac{\partial \theta}{\partial t} = D_z \frac{\partial^2 \theta}{\partial z^2} , \qquad /2/$$

with a view to

$$\theta = \frac{V_w}{V} \quad \text{and} \quad f = \frac{d\, V_w}{dt} , \qquad /3/$$

equation /2/ was obtained as follows:

$$\frac{f}{V} = D_z \frac{\partial^2}{\partial z^2} \;/\; \frac{V_w}{V} \;/ , \qquad /4/$$

Then both sides of Eq • /4/ were differenciated in relation to time and the following was obtained:

$$\frac{\partial}{\partial t} \;/\; \frac{f}{V} \;/ = \frac{\partial}{\partial t} \left[D_z \frac{{}^{2}}{z^2} \;/\; \frac{V_w}{V} \;/ \right], \qquad /5/$$

As it was assumed that volume /V/ of the investigated porous medium is constant /V = const/ so:

$$\frac{\partial f}{\partial t} = D_z \frac{\partial^2}{\partial z^2} \;/\; \frac{\partial V_w}{\partial t} \;/ , \qquad /6/$$

Finally Eq • /6/ was obtained in which infiltration rate is the function of time /t/ and coordinate /z/:

$$\frac{\partial f}{\partial t} = D_z \frac{\partial^2 f}{\partial z^2} , \qquad /7/$$

The following boundary conditions were assumed:

$$f = f_o \quad \text{for} \quad z = 0 \quad \text{and} \quad t = 0 , \qquad /8/$$

$$f = f_c \quad \text{for} \quad z = 0 \quad \text{and} \quad t \longrightarrow \infty , \qquad /9/$$

Particular solution of Eq • /7/ for these boundary conditions can be expressed in the form:

$$f\ /t/ = f_c + /f_o - f_c/ \cdot e^{-kt}, \qquad /10/$$

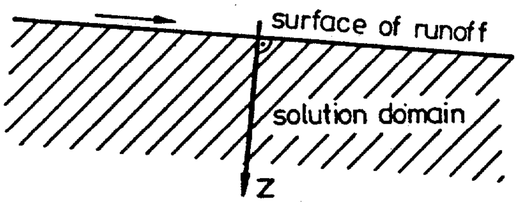

Fig. 1. Definition sketch for equation /7/

as well known Horton equation /Horton, 1940/.

In order to approximate surface runoff rate it is convenient to transform the direction of coordinate by values t_o and f_c, Figure 2.

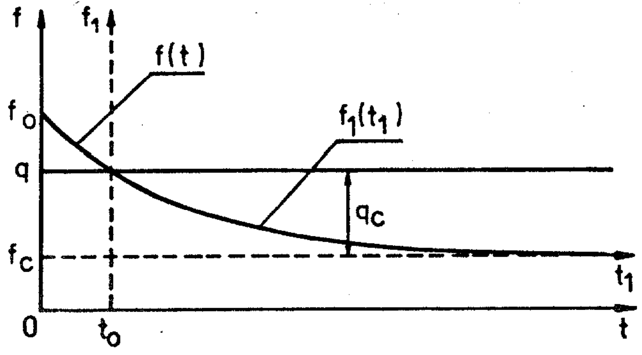

Fig. 2. Function of infiltration rate in time

In the transformed coordinate system the following relationships were received:

$$q_c = q - f_c \, , \qquad /11/$$

$$t_1 = t - t_o \, , \qquad /12/$$

with regard to

$$q_s \, /t_1/ \; = \; q_c - f_1 \, /t_1/ \quad , \qquad /13/$$

After transformation of Eq . /10/ surface runoff rate was obtained:

$$q_s \, /t_1/ \; = q_c \, /1 - e^{-kt_1} \, /, \qquad /14/$$

The value q_c can be defined as follows:

$$q_c = \psi \cdot q \ , \qquad /15/$$

where ψ is constant coefficient of runoff from the stack at a point when the rate of runoff approaches constant value q_c. Taking into account Eq. /15/ the volume of runoff Vs for any time t_1 can be calculated by integrating Eq. /14/ :

$$V_s\ /t_1/ = \int_0^{t_1} \left[\psi \cdot q\ /1 - e^{-kt_1}/ \right] dt_1 \ , \qquad /16/$$

as a result we obtain

$$V_s/t_1/ = \psi \cdot q \left[t_1 - \frac{1}{k}\ /1 - e^{-kt_1}/ \right] , \qquad /17/$$

The coefficients k and ψ are the function of rainfall rate /q/ and stack parameters /W, β , P /.

$$k = f_1\ /q, W, \beta , P/ \ , \qquad /18/$$

$$\psi = f_2\ /q, W, \beta , P/ \ , \qquad /19/$$

The formulae were qualified on the base of the experimental investigations.

As the values of runoff and concentration of suspension depend on initial parameters q, β , W and P /Rydzyński 1981/, the general equation of suspension concentration can be expressed in the dimensionless form:

$$Y = \frac{S\ /t_1/}{S_{max}} = f\ /kt_1/ \ , \qquad /20/$$

Coefficient k integrates the value of runoff and concentration of suspension. The particular form of function f was experimentally qualified.

EXPERIMENTAL RESEARCH

Experimental researches were carried out at the Water Engineering Institute of Technical University in Szczecin . The hydraulic model was designed by author. It consists of rainfall simulator and laboratory stack of 3,0 m^2 projection area which is situated underneath. Fresh phosphogypsum from the plant was placed on the draining plate of stack. The laboratory stack enables to obtain variations of runoff surface slope within the range 0 - 60 % and the rainfall simulator produces rain of a wide range of intensity.

Water cycle on the model was the following, Figure 3 : Upper tank 1 was supplied from municipal water - pipe net -

work. Water flowed with constant intensity from tank 1 to measuring tank 2. Excess water from the upper tank flowed to the lower tank. Water from tank 2 flowed by overfalls to rainfall simulator 3 and into the stack model 4. Excess water from the simulator was directed to measuring tank 9. Some rainfall and phosphogypsum were directed to runoff channel 5 from which samples were taken to investigate concentration of runoff contamination. Runoff from channel 5 was directed to measuring tank 6 of runoff rate.

The rest of the rainfall infiltrated into the stack finding its way to infiltration water channel 7 and then to measuring tank for infiltration waters 8.

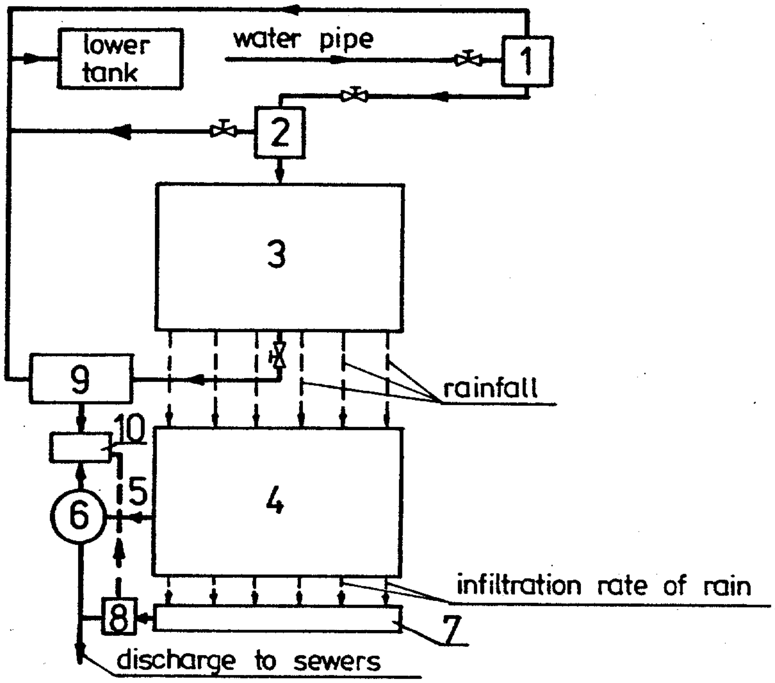

Fig. 3. Scheme of laboratory model

1. Upper tank, 2. Measuring tank at inflow, 3. Rain simulator, 4. Erosion simulator, 5. Runoff channel, 6. Runoff measuring tank, 7. Channel of infiltration waters, 8. Infiltration measuring tank, 9. Measuring tank at outflow, 10. Measuring system

Researches were carried out in two series. During the first series the runoff rate and concentration of suspension in the runoff were measured. The rainfall intensity was constant. Investigations were made for phosphogypsum produced mainly on the base of Florida and Morocco phophorites. In the second series at the varied rainfall intensity the suspension concentration was measured as well as sulfates, phosphates, fluorides, ammonia nitrogens, iron and pH. This series of investigations was carried out for phosphogypsum produced mainly on the base of Kola apatites.

Phosphogypsum was placed on the model in layers of equal thickness without any compacting. The layer of medium grain size sand and sized gravel was situated underneath. It served as drainage and was supposed to eliminate phosphogypsum slip at the stack bottom plate.

In every first experiment the stack material was compacted due to rainfall. As a result parameters of natural moisture /W/ and porosity /n/ changed. Parameters of rainfall intensity /q/ and stack surface slope / β / were changed before every experiment.

Most experiments were carried out with phosphogypsum compacted by rainfall. It corresponds with conditions of real stack where compacted area /due to rainfall and means of transport/ is much larger than the area taken up by fresh phosphogypsum coming directly from production line which has great porosity.

DEFINING THE NUMBER OF EXPERIMENTS

It was difficult to plan experimental investigations as the initial stack parameters namely natural moisture /W/ and parameter P were measurable variables but they were not fully controlled.

Identification of runoff equation coefficients and suspension concentration distributions was made in the course of experiments. It was assumed that approximated polynomials of which terms are measured variables q, P, W and β would be the mathematical form of the desired equations. The number of necessary experiments was determined basing on the following assumptions:

- the number of measurable variables is $i = 4$ /q, P, W, β /,
- approximated polynomials of the second degree at the outmost can be used for practical defining coefficients of the required equations.

Taking into account the above mentioned assumptions we can write the general form of equation which defines e. g recession coefficient k as:

$$k = b_o + \sum_{n=1}^{n=4} b_n x_n + \sum_{n=1}^{n=4} b_{nn} x_n^2 + \sum_{n \neq l}^{1 \leq n,l \leq 4} b_{nl} x_n x_l \quad , \qquad /21/$$

where the number of coefficients b to be defined is 15 a maximum. In this case the number-of independent equations should be $N_b = 15$, therefore the number of experiments should be the same.

In the first series of investigations the author performed and described 18 experiments dealing with surface contamination runoff.

RESULTS OF EXPERIMENTS

Table I presents main parameters of runoff volume equation for the first series of experiments. Standard deviation σ was taken as the measure of accuaracy.

Substituting values q, k, ψ , to from table I to equations /14/ and /17/ we obtain the rate and volume of runoff from stack model. Its projection area onto the horizontal plane is 3,0 m^2. According to the analytical model assumptions the rate and volume of runoff from any surface can be calculated basing on the principle of superposition of runoff rate and volume from unit surface /1 m^2/.

Using approximation polynomials the coefficients k and ψ were defined as initial parameter q, W, β and P. In table II values of these parameters are presented.

There were two stages of calculations. At the first stage regression equations regarding the whole investigated range q, W, β and P were calculated. Phosphogypsum compacted and non-compacted by rainfall was considered /Rydzyński, 1984/. At the second stage regression equations were worked out only for the compacted phosphogypsum /experiments No 4, 7, 11, 15 were omitted/ for the sake of practical use of experimental results. Residual error σ and multiple correlation coefficient ρ of estimated parameters k and ψ were taken as accuracy measure of regression equations. These measures are given under each regression equation. Regression equations take into account only compacted phosphogypsum:

$$k = -\,6{,}400 + 0{,}232\ W + 0{,}0000119\ q^2 - 0{,}00187\ W^2 - \\ + 0{,}000177\ \beta^2 + 0{,}000182\ W \cdot \beta - 0{,}000452\ W \cdot P \quad [\mathrm{min}^{-1}]\ , \qquad /22/$$

where $\sigma = \pm\ 0{,}057\ \mathrm{min}^{-1}$, $\rho = 0{,}987$,

$$\psi = 0{,}803 - 0{,}00114\ W^2 + 0{,}000272\ q \cdot W - 0{,}000480 q \cdot P + \\ + 0{,}00134\ W \cdot \beta + 0{,}00202\ W \cdot P - 0{,}00286\ \beta \cdot P, \quad /23/$$

where $\sigma = \pm\ 0{,}046$, $\rho = 0{,}987$

Approximation of coefficients k and ψ with the use of the first degree polynomials is presented in the paper /Rydzyński, 1981/.

On the base of experiments a simple form of suspension concentration distribution was defined, Eq. 20 which can be applied in practice:

$$Y = \frac{S/t_1/}{S_{max}} = A \cdot x \cdot e^{-Bx} \qquad /24/$$

Table I. Main parameters of runoff volume equation for particular experiments

Number of experiment	ψ	q [$cm^3 min^{-1}$]	k [min^{-1}]	t_o [min]	Range of runoff volume V_s /t_1/ [cm^3]	Standard deviation σ [cm^3]
1	0,742	3420,0	0,7440	0,00	0-20000	± 507,00
2	0,438	3288,0	2,1600	0,00	0-20000	± 345,0
3	0,370	1446,0	0,1850	0,00	0-20000	± 88,2
4*	0,0876	3660,0	0,0273	8,50	0-21640	± 355,5
5	0,437	4164,0	1,1160	0,00	0-20000	± 287,2
6	0,708	4062,0	0,6660	0,00	0-20000	± 81,2
7*	0,277	2717,4	0,0200	4,00	0-17420	± 169,3
8	0,253	2260,8	0,1132	1,00	0-22490	± 235,4
9	0,176	1657,2	0,0407	3,00	0-23460	± 182,4
10	0,375	2112,6	0,2450	0,00	0-20000	± 190,1
11*	0,355	2400,0	0,0370	9,00	0-18190	± 168,1
12	0,177	1047,0	0,06390	0,75	0-23050	± 265,4
13	0,166	1023,6	0,04230	1,50	0-22190	± 354,0
14	0,395	2065,2	0,20660	0,00	0-18260	± 136,0
15*	0,122	2534,4	0,01190	32,20	0-21650	± 260,3
16	0,201	1721,4	0,0140	3,50	0-22990	± 401,0
17	0,270	1483,2	0,1680	0,00	0-20430	± 258,9
18	0,447	1653,0	0,3370	0,00	0-22660	± 167,4

* - denotes experiment for fresh phosphogypsum

Table II. Initial parameters of rainfall intensity /q/, natural moisture /W/, stack slope/β/ and parameter P

Number of experiment	q [dm^3 / s • ha]	W [%]	β [%]	P [%]
1	190,0	62,3	19,5	22,6
2	182,7	45,8	9,8	25,5
3	80,3	52,7	9,8	23,6
4^{*}	203,3	49,6	19,5	49,0
5	231,3	43,8	24,4	34,1
6	225,7	60,4	12,2	30,5
7^{*}	150,7	56,5	28,7	51,2
8	125,6	66,2	34,15	32,8
9	92,1	49,9	39,0	29,4
10	117,4	67,1	43,9	29,2
11^{*}	133,2	52,8	48,8	42,3
12	58,2	61,5	53,7	30,5
13	56,9	58,2	58,5	29,1
14	114,7	61,2	59,9	28,6
15^{*}	140,8	42,1	19,5	51,0
16	95,6	67,5	9,8	31,9
17	91,8	62,4	24,4	28,0
18	82,4	56,5	14,6	28,5

* - denotes experiment for fresh phosphogypsum

where: $x = kt_1$; A i B dimensionless coefficients of function Y.

Equation /24/ has the following features:

- for $x = kt_1 = 0$·

$$\frac{S\,/t_1/}{S_{max}} = 0 \qquad /25/$$

- for definite $x = kt_1 = \frac{1}{B}$ reaches maximum value

$$\frac{S\,/t_1/}{S_{max}} = 1, \qquad /26/$$

wchich reduces equation /24/ to the form:

$$Y = B \cdot x \cdot e^{1 - Bx} \qquad /27/$$

for $x = kt_1 \longrightarrow \infty$

$$\frac{S\,/t_1/}{S_{max}} \longrightarrow 0 \;, \qquad /28/$$

It results from Eq. /28/ that when the time of runoff tends to infinity the values of contamination concentration approach zero. Regarding the fact that in practical calulations of concentration distribution the maximum considered time of runoff is several hours, equation /27/ can be used for approximation of concentration distribution. It can be written in the dimensional form as follows:

$$S\,/t_1/ = S_{max} \cdot B \cdot kt_1 \cdot e^{1-Bkt_1} \quad [\,g/dm^3\,] \;, \qquad /29/$$

Table III presents main parameters of equation /29/ in particular experiments. As accuracy measure of the discussed dependency was taken standard deviation σ.
S max and B were defined as functions of initial parameters q, W, β and P with the use of approximation polynomials. Calculations were made at two stoges similarly to the case of coefficients k and ψ.

$$S_{max} = 150{,}9 - 14{,}78 \quad + 0{,}065q^2 + 0{,}354W^2 - 0{,}0225\,\beta^2 +$$
$$- 0{,}368q \cdot W + 0{,}268q \cdot \beta \quad [\,g/dm^3], \qquad /30/$$

where $\sigma = \pm 22{,}9 \quad [\,g/dm^3\,]$, $\qquad \rho = 0{,}985$

$$B = -0{,}466 - 0{,}0670\,\beta - 0{,}0000158q^2 + 0{,}00449W^2 +$$
$$+ 0{,}000890\,\beta^2 + 0{,}0213P^2 - 0{,}0185\, W \cdot P \;, \qquad /31/$$

where $\sigma = \pm 0{,}122$, $\qquad \rho = 0{,}985$.

Suspension load at any time t_1 can be expressed as a product of runoff rate, Eq. /14/ and suspension concentration, Eq. /29/:

Table III. Main parameters of equation of suspension concentration distribution in particular experiments

Number of experiment	S_{max} [g/dm^3]	B	Range of suspension concentration $S/t_1/$ [g/dm^3]	Standard deviation δ g/dm^3
1	216,7	0,256	96,2 - 216,7	± 21,6
2	43,7	0,0404	23,3 - 43,7	± 4,2
3	67,4	0,271	26,4 - 67,4	± 5,8
4*	100,4	0,206	34,8 - 100,4	± 12,2
5	361,8	0,146	130,6 - 361,8	± 64,0
6	308,3	0,192	97,4 - 308,3	± 45,3
7*	301,4	1,017	138,9 - 301,4	± 45,2
8	271,2	0,445	169,5 - 271,2	± 46,6
9	246,4	0,629	143,4 - 246,4	± 30,3
10	457,8	0,379	233,0 - 457,8	± 102,5
11*	401,5	0,991	190,7 - 401,5	± 45,8
12	382,1	0,533	155,5 - 382,1	± 46,3
13	283,8	0,597	173,1 - 283,8	± 55,9
14	626,9	0,336	339,8 - 626,9	± 90,3
15*	204,7	1,691	91,5 - 204,7	± 38,3
16	105,0	1,237	54,0 - 105,0	± 20,6
17	152,2	0,335	61,3 - 152,2	± 15,7
18	167,1	0,193	108,4 - 167,1	± 17,0

* - denotes experiment for fresh phosphogypsum

$$L/t_1/ = 0{,}06\,\psi \cdot q \cdot F \cdot S_{max} B k t_1 e^{1-Bkt_1} \cdot /1 - e^{-kt_1}/ \quad [\text{kg/min}] \quad , \quad /32/$$

Integrating, Eq. /32/ in relation to time /t1/ the total suspension load in a given volume of runoff M/t1/ can be defined according to the following equation:

$$M\,/t_1/ = 0{,}06\,\psi \cdot qFS_{max}Bke \left\{ -\,/1 + Bkt_1/ \cdot \frac{e^{-Bkt_1}}{B^2 \cdot k^2} + \right.$$
$$+ \frac{e^{-/B+1/kt_1}}{/B+1/^2 \cdot k^2}\,[\,/B+1/\,kt_1 + 1\,] + \frac{1}{B^2 \cdot k^2} +$$
$$\left. - \frac{1}{/B+1/^2 \cdot k^2} \right\} \quad [\,kg\,]\,, \qquad /33/$$

Particular values in equations from Eq. /29/ to Eq. /33/ have the following dimensions:

F - [ha] , q - [$dm^3/s \cdot ha$] , S_{max} - [g/dm^3], t_1 - [min] , k - [min^{-1}] , ψ , B - [dimensionless] .

The second series of experiments followed preliminary field surveys where suspension concentration were measured as well as sulphates, phosphates, fluorides, ammonia nitrogen, iron, pH and chemical oxygen demand. Also preliminary investigations on concentration of the above mentioned contamination indicators in rainfall were carried out. The measurements were made in proximity of the phosphogypsum stack, Figure 4.

As a result of rainfall and water fluctuations in the neighbouring water courses, contaminations from phosphogypsum stack are washed out and flow in an uncontrolled way to surface and ground waters. Most of rim d-itches were damaged due to squeezing out part of the peat from under the stack base. Some water from the stack flows to local depressions, the rest flows in an uncontrolled way to neighbouring surface waters, Figure 4.

In order to define the degree of water environment pollution, water samples were taken from the rim ditch P.2 surrounding the old part of stack and from the local depression P.1 situated near the stack where phosphogypsum is put away at present. Results of these studies are presented in Tab.IV In the case of samples P.1 and P.2 water from phosphogypsum stack is extremely concentrated as there is an additional chemism of ground waters occuring high in the peat layer. In case of sample D.1 we have a view on the amount of contamination concentration in the rainfall. Prom all these investigations we can draw conclusions regarding air pollution in the neighbourhood of the Ch. P. "Police".

Contamination concentrations presented in Tab. IV do not inform us directly about the amount of contamination concentrations in the surface runoff alone. It is important to know the amount of runoff from stack and its contamination in order to design draining and treatment as well as utilization of the water. Therefore in the second series of studies 26 laboratory experiments were made with surface runoff from phosphogypsum stack.

Table IV. Results of field investigations on surface and rain water samples taken in proximity in phosphogypsum stack

Indicator of contamination	P.1	P.2	D.1
pH	1,6 ÷ 1,8	2,4	5,0 ÷ 5,8
Suspension [mg/dm^3]	30 ÷ 60	95,0	< 30
Fe, [mg/dm^3]	175 ÷ 244	156,0	1,0 ÷ 2,0
$N_{NH_4^+}$, [mg/dm^3]	2,7 ÷ 21,5	30,8	0,22 ÷ 0,25
PO_4^{-3}, [mg/dm^3]	38400 ÷ 66000	53000	10,0 ÷ 20,3
SO_4^{-2}, [mg/dm^3]	3400 ÷ 7100	2060	44 ÷ 68,0
F^-, [mg/dm^3]	780,0 ÷ 840,0	198,0	0,18 ÷ 1,20
COD, [mgO_2/dm^3]	249 ÷ 322	178,0	51,0

Phosphogypsum was produced mainly from Kola apatites . One charge of fresh phosphogypsum was used for every set of five experiments. For those experiments the range of rain - fall rate was from 16,0 - 191 $dm^3/s \cdot ha$ /6,5 - 77,3 $dm^3/s \cdot acre$/.

In Tab. V are given exemplary results of contamination concentrations in surface runoff.
In future the author intends to describe the mathematical model of variations of load concentrations in time as a function of rainfall rate and parameters of phosphogypsum stack.

Table VI presents initial parameters q, W, β , P, n, t and t_0 which were used for making exemplary experiments.

APPLICATION OF INVESTIGATION RESULTS

In order to apply investigation results contamination loads flowing to surface waters with the runoff from phosphogypsum stack neglected so far, were defined.
Calculations were made for the stack of Ch. P. "Police".
Stack projection area was determined basing on the map made according to measurements from April 1981.
Stack location plan is shown in Fig. 4.

Table V. E Exemplary results of contamination concentrations in surface runoff from phosphogypsum stack for the second series of laboratory research

Number of experiment	pH min-max	Suspension min-max [g/dm^3]	Fe min-max [mg/dm^3]	$N_{NH_4^+}$ min-max [mg/dm^3]	PO_4^{-3} min-max [mg/dm^3]	SO_4^{-2} min-max [mg/dm^3]	F^- min-max [mg/dm^3]
11*	1,8-3,0	82-211	1,1-46,1	0,68--1,24	1680--15420	765--1660	2,3-7,2
12	3,6-6,2	167-326	0,13-6,4	0,80--1,84	35-769	1100--1760	3,6-6,2
13	5,4-6,4	164-217	0,07-1,4	0,28--1,07	17-127	1150--2360	14,1--22,3
14	4,2-4,8	156-369	0,12--1,05	0,29--1,05	23-162	762--1530	0,6-1,4
15	4,1-6,3	45-317	0,12--2,09	0,68--1,44	11-101	1100--1670	5,6--10,5

* - denotes experiment for fresh phosphogypsum

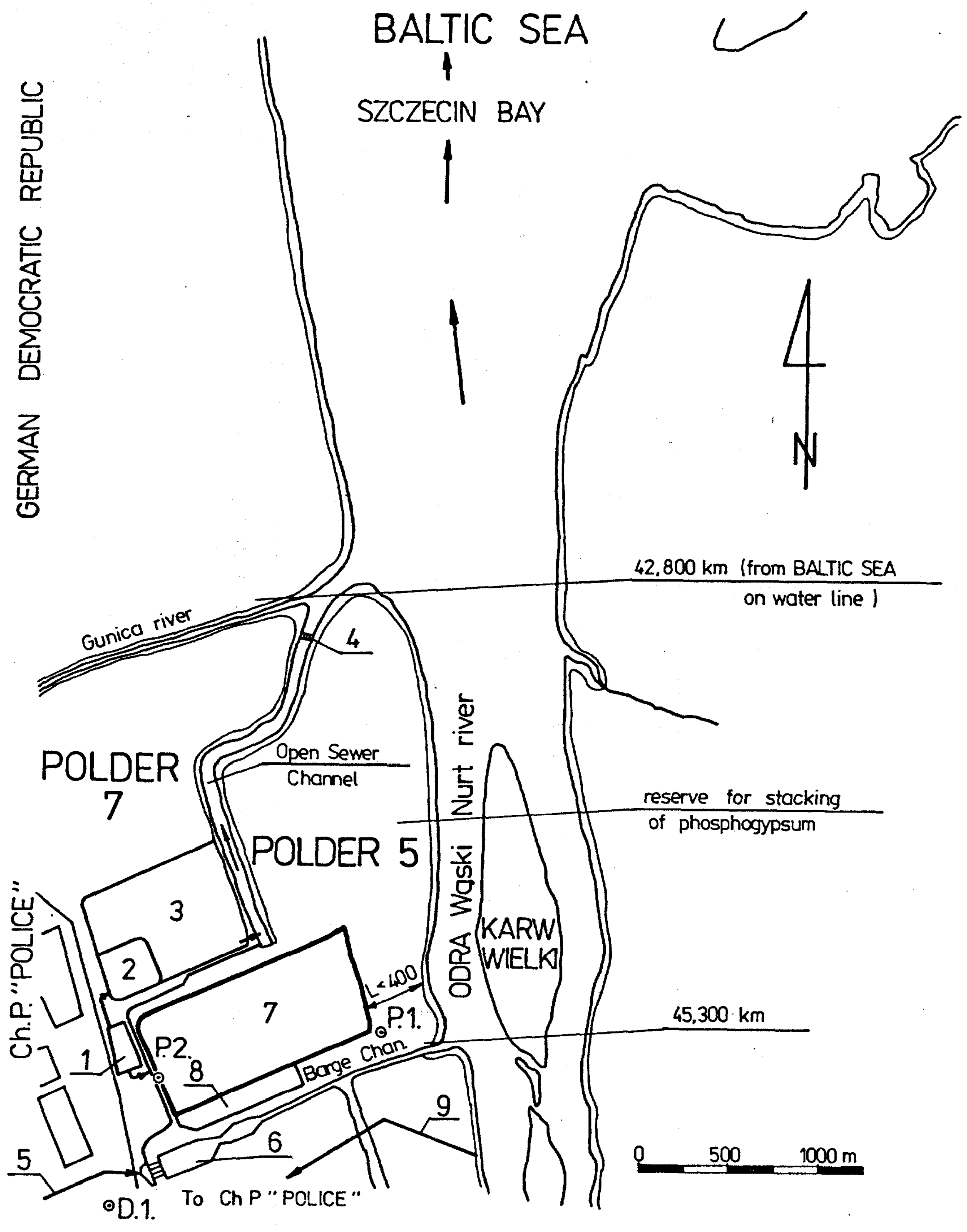

Fig. 4. Ch.P. "POLICE" Phosphogypsum Stack

1. Chemical Treatment Station ; 2. Lagoon ; 3. Storage - Settling Tank ;
4. Outlow of Sewer Channel ; 5. Channel of storm and cooling water ;
6. Barge Port ; 7. Phosphogypsum dry stack ; 8. Settling Tank for fly-ash ;
9. Water Intake for Cooling ; ⊙ P1, P2 - samples of water from stack ;
⊙ D.1 - sample of rainfall .

Table VI. Exemplary results of initial parameters q, W, β , P, n, t and t_o for the second series of laboratory research

Number of experiment	q [$dm^3/s \cdot ha$]	W [%]	β [%]	P [%]	n [%]	t [min]	t_o [min]
11*	135,6-98,5	86,3	40,0	53,8	75,2	151,0	36,2
12	39,4	104,6	45,0	40,8	71,1	52,2	0,0
13	88,8-71,1	98,7	50,0	36,8	68,2	23,2	0,0
14	68,2	96,8	45,0	36,8	67,9	50,0	0,0
15	83,5-21,6	98,8	55,5	35,9	67,7	39,8	0,0

* - denotes experiment for fresh phosphogypsum

At that time general stack area was about 78 ha. For the porpose of calculations the stack was divided into three parts.

- The first part was the area of about 12,8 ha with steep hills. The mean slope was about 58 % / $\alpha \cong 30^{o}$ /,
- The second part /the stack top/ with the area of about 47 ha was mainly flat with local concavities and elevations. Runoff from this part was meaningless for practical purposes so it was not taken into account.
- The third part was the area of about 18,2 ha with slope range from 3 to 15 %, situated at the foot of the stack steep hills.

For the purpose of runoff calculations only two parts of the stack were considered, namely:

$F_1 = 12{,}8$ ha with the slope $\beta_1 = 58$ %,

$F_2 = 0{,}7 \cdot 18{,}2 = 13$ ha with the slope $\beta_2 = 10$ %.

The other initial parameters taken for the computational model were as follows:

- natural moisture $W_1 = W_2 = 55$ %,
- porosity $n_1 = n_2 = 53$ %,
- parameter P according to Eq. /1/ P = 27 %,
- probability of rainfall p = 10 %,
- mean rainfall a year H = 557 mm,
- time of rain t = 68 min /Rydzyński, 1984/,
- intensity of rain $q = f\,/t, p, H/ = 61\ dm^3/s \cdot ha$.

Coefficients k, ψ, S max were defined according to equations /Rydzyński, 1981/:

$$k = 0{,}62 + 0{,}0039q + 0{,}0012W + 0{,}00038\beta - 0{,}031\,P \quad [\,min^{-1}], \qquad /34/$$

$$\psi = 0{,}74 + 0{,}0032q - 0{,}026P, \qquad /35/$$

$$S_{max} = -\,45{,}4 + 1{,}24q + 7{,}95\beta - 2{,}49\,P\ [\,g/dm^3], \qquad /36/$$

Substituting initial parameters, the following values of coefficients were obtained:

- $k_1 = 0{,}9\ min^{-1}$ $k_2 = 0{,}08\ min^{-1}$, mean $k = 0{,}09\ min^{-1}$
- $\psi_1 = \psi_2 = 0{,}24$
- $S_{max_1} = 423\ g/dm^3$, $S_{max_2} = 42\ g/dm^3$

Maximum rate of runoff and the total volume of surface runoff area are:

$$q_s/t_1 = t/ = 3{,}6\,\psi \cdot q\,/F_1 + F_2/\,/1 - e^{-kt_1}/ = 1360\ m^3/h \qquad /37/$$

$$V_s/t_1/ = 0{,}06 \cdot q\ /F_1 + F_2/\ [\ t_1 - \frac{1}{k}\ /1 - e^{-kt_1}/\ ] = \\ = 1290\ m^3 \qquad /38/$$

To determine the mean load of suspension in the runoff calculations were simplified by taking the mean suspension concentration from areas $S_1 = 211$ g / dm^3 and $S_2 = 21$ g / dm^3.
Thus the mean concentration can be defined as:

$$S = \frac{S_1 \cdot F_1 + S_2 \cdot F_2}{F_1 + F_2} = 116\ g/dm^3, \qquad /39/$$

Total mass of suspension contained in the runoff volume is:

$$M\ /t_1/ = V_s\ /t_1/ \cdot S = 150\ 000\ kg, \qquad /40/$$

an the mean load of suspension:

$$L\ /t_1/ = \frac{M\ /t_1/}{t_1} = 132\ 700\ kg/h\ , \qquad /41/$$

It is especially important to know suspension load when designing and exploiting rim ditches around the stack.

In order to determine the hazard of polluting Szczecin Bay by the very runoff from phosphogypsum stack, the calculated loads were compared with ultimate contamination loads for all sorts of waste water coming from Ch. P. "Police",Table VII. In the same table were compared concentrations of selected contamination indicators contained in the runoff from phosphogypsum stack with ultimate concentrations for the highest and lowest class of surface water purity in Poland.
It should be noted that at present contamination loads in surface runoff are remarkably greater than those given in Tab. VII due to the extension of phosphogypsum stack area.

CONCLUSIONS

- The paper presents. computational model and laboratory studies on suspension surface runoff from dry phosphogypsum stacks. On the model the amount of runoff and suspension concentration were dependent on rainfall intensity /q/ and physical parameters of stack such as: stack slope /β/,porosity /n/ and natural moisture /W/.

Table VII. Selected contamination loads in runoff drained from phosphogypsum stack into surface water

Indicator of contamination	Rain wastes from phosphogypsum stack			Class of surface water purity		Ultimate contamination loads for all sorts of waste water from Ch. "Police"	
	Q $[m^3/h]$	concentration S $[mg/dm^3]$	load L [kg/h]	I $[mg/dm^3]$	III $[mg/dm^3]$	Q $[m^3/h]$	Load [kg/h]
Phosphates - PO_4^{-3}	1360	200	272	0,2	1,0	12971	9,6
Sulphates - SO_4^{-2}		2000	2720	150	250		5058
Fluorides - F^-		20	27,2	1,5	2,0		83,1
Iron - Fe		10	13,6	1,0	2,0		13,6
Ammonia nitr. - $N_{NH_4^+}$		2	2,7	1,0	6,0		17,5
Chem.Oxyg.Dem. COD - O_2		180	245	40	100		307
pH		1,8-6,4		6,5-8,0	6,0-9,0		7,0-9,0

- Furthermore investigations were carried out to define amounts of selected indicators of contamination such as:phosphates, sulfates, fluorides, iron, ammonia nitrogen, chemical oxygen demand and pH in the runoff from phosphogypsum stack.
- Studies proved that during rainfall the load of phosphate /270 kg PO_4/h/ which is the most essential indicator from water protection point of view exceeds considerably ultimate load of phosphates /10 kg PO_4/h/ for all sorts of waste water from Chemical Plant "Police". The ultimate load of phosphates was determined to protect Szczecin Bay from eutrophication.
- Presented studies can be of use for designing and exploiting engineering equipment for draining, collecting, purification an utilization of rain wastes coming from the phosphogypsum stacks.

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REFERENCES

Eagleson, P. S. 1970. Dynamic hydrology. Mc Graw-Hill, Inc. U.S.A.

Horton, R. E. 1940. An approach toward a physical interpretation of infiltration capacity. Proc. Soil Sci. Soc. Am. 5: 399 - 417.

Rydzyński, R. 1981. Wielkość spływu powierzchniowego zanieczyszczeń nierozpuszczalnych z terenów składowisk przemysłowych na przykładzie składowiska fosfogipsów /doctor's thesis/. Technical University of Szczecin.

Rydzyński, R. 1984. Spływ powierzchniowy zanieczyszczeń ze składowiska fosfogipsów. Archiwum Ochrony Środowiska.1 : 85 - 104.

Rydzyński, R. 1986. Erosion from industrial waste heaps . International Conference "Hydrological Processes in the Catchment". Cracow, 8-11 May 1986: 153 - 158.

PHOSPHOGYPSUM DISPOSAL : BENEFITS OF NEUTRALIZATION OF THE TAILING PRODUCT

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INTRODUCTION

Any strongly acidic waste material presents potential problems for disposal, both in the primary handling of the material and in its subsequent secondary or resultant effects. Phosphogypsum is no exception and is in many respects, a particularly difficult waste in that it contains an extremely chemically aggressive acid, hydrofluoric acid. In determining possible problems for the disposal of phosphogypsum, there are two principal factors which must be considered :

- the high pollution potential of the waste and
- chemical attack of the waste on natural materials.

To overcome these problems it is usual for disposal sites to be lined either with an engineered clay liner or an artificial liner.

In 1974 Triomf Fertilizers (Pty) Ltd constructed the largest phosphoric acid plant in southern Africa at Richards Bay on the north coast of Natal. Following evaluation of the alternatives Triomf decided to dispose of the phosphogypsum waste in a land based facility using a tailings impoundment constructed of slurried phosphogypsum. There is a shortage of suitable land for industrial development in Richards Bay and a site was therefore provided in a nearby low lying swamp. Since the environmental and hydrological conditions at the site were critically balanced, the possibility of accidental discharge of acid effluent into the Bay was unacceptable to the authorities. This factor and the practical difficulties associated with providing a suitable liner over the marshland, resulted in a decision to neutralize the tailings with slaked lime at the factory, before transporting the tailings to the impoundment.

This paper summarizes the results of investigations undertaken to evaluate the environmental benefits of neutralization and the engineering properties of the product.

NEUTRALIZATION OF THE TAILINGS

The manufacture process yields orthophosphoric acid, phosphogypsum, hydrofluoric acid and hydrofluorsilicic acid. The acids render the phosphogypsum waste highly acidic.

Neutralization is achieved by the addition of slaked lime and the neutralization reaction takes the general form :

$$H_2SiF_6 + 3Ca(OH)_2 \rightarrow SiO_2 + 3CaF_2 + 2H_2O$$

In this way fluorine is removed from the reaction by the precipitation of calcium fluoride and other complex fluoride compounds which have low solubility and are stable.

GEOTECHNICAL PROPERTIES OF NEUTRALIZED PHOSPHOGYPSUM

An extensive investigation programme has been carried out to measure the geotechnical properties of the neutralized phosphogypsum. Comparison of the results with the properties of the acid phosphogypsum produced from the same source rock shows the following :

- the grading envelopes of the products are similar;
- the permeability of the tailings is controlled primarily by the production process, the crystal dimensions and the method of placement. Neutralization appears to have little influence on the permeability of the tailings;
- the shear strength of the neutralized product is marginally lower than that of the acid phosphogypsum;
- the consolidation properties of both products are similar.

Neutralization of the tailings therefore has been shown to have little influence on the geotechnical properties of the product.

BENEFITS OF NEUTRALIZATION

The following benefits of neutralization have been identified by the experimental work and the experience gained during operation of the impoundment :

1 Reduction in Pollution Potential

It is a property of all acid wastes that in addition to their low pH values, they also display high values of other chemical species in their liquid phases. In phosphogypsum slurry the species liable to cause pollution, because of their elevated concentrations and chemical mobility, are total dissolved solids (TDS), sulphate, phosphate and fluoride. Tests on samples of neutralized phosphogypsum leachate have shown that the concentrations of these species are significantly reduced. The measured concentrations have been compared with standards giving the maximum permissible concentrations for discharge of effluent into a watercourse or groundwater. It is apparent that concentrations of many species in the acid phosphogypsum are hundreds and even thousands of times greater than the permissible levels, whilst seepage water from the neutralized product has levels close to the acceptance limits.

At the Richards Bay impoundment the licensing authorities required that boreholes be sited around the impoundment to allow the quality of the marsh water to be regularly monitored. Tests on water samples recovered from these boreholes have shown that all chemical species have remained within base line values.

2 Reduction of Chemical Attack on Natural Materials

Hydrofluoric acid has the unique capacity of dissolving silicates. The main attack product is hydrofluorsilicic acid, an aqueous phase, which often appears as a semi-gelatinous colloid material.

In phosphogypsum disposal the environmental consequences resulting from hydrofluoric acid attack are serious and experience suggests that the following may occur :

- failure of soil or artificial liners under facilities resulting in seepage of highly polluting liquid into the groundwater regime;
- physical failure of starter walls, embankments and solution trenches, resulting in a loss of phosphogypsum effluent to the environment;
- clogging of underdrains and toe drains leading to uncontrolled seepage and possible stability problems.

Triaxial leaching tests were carried out by the author on sandy silts used to line an acid phosphogypsum impoundment. These showed that acid attack occurred. Initially it was found that the permeability of the silt samples increased by one order of magnitude. Continued leaching with acid effluent resulted in precipitation and a reduction in permeability. Many of the attack products were water soluble. Tests carried out using neutralized effluent showed that the permeability of the samples reduced appreciably with leachate seepage.

Triaxial compression tests were carried out on the leached samples. The results showed that the secant modulus of the acid attacked samples had increased appreciably i.e. the ductility of the materials had decreased. These results suggest that liners constructed with these materials become brittle as a result of acid attack and would crack if the foundation soils settle under the impoundment loading. Only a small increase in secant modulus was measured for the samples subjected to leaching with neutralized effluent.

3 Vegetation of the neutralized phosphogypsum

The impoundment at Richards Bay is located in an area surrounded by thickly vegetated marshland. Within one year of commencing disposal it was apparent that the neutralized phosphogypsum would support vegetation since naturally seeded plants began to appear on inactive surfaces of the embankment. Since that time the vegetation cover has multiplied to the extent that the entire embankment, with the exception only of the active and most recently placed tailings, is thickly covered by naturally seeded plants.

The abundant vegetation at the Richards Bay impoundment may be attributed to the following factors :

- neutralization of the tailings:
- lime acts as a "conditioner" to materials which contain no organic matter:
- reduction in salt content:
- the presence of small quantities of phosphoric acid within the tailings:
- the sub-tropical climate at Richards Bay.

The vegetation cover has resulted in a very significant reduction in the visual impact of the impoundment.

CONCLUSIONS

Experience at the Richards Bay impoundment has shown that neutralization of the phosphogypsum tailings has led to the following benefits :

- reduction in the pollution potential of the tailings:
- reduction of chemical attack on soils and artificial liners and soils used to construct the impoundment;
- creation of conditions suitable for vegetation of the impoundment.

The geotechnical properties of the tailings are unaffected by the neutralization process.

PRODUCTION, UTILIZATION RESEARCH, AND MANAGEMENT

WORLDWIDE PRODUCTION AND UTILIZATION OF PHOSPHOGYPSUM

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INTRODUCTION

By 1980, annual production of phosphogypsum was in the 120-150 million metric ton (mmt) range. A 1981 survey of companies producing phosphogypsum showed 14% of all phosphogypsum was being reprocessed, 58% was stored, and 28% was being dumped. This magnitude of wasted phosphogypsum means reprocessing options must be further explored.

Interest in development of phosphate resources and in phosphoric acid processing facilities runs high in third-world countries. Table 1 lists third world countries which are major producers of phosphate rock and/or P_2O_5. Almost all of these countries are both planning new P_2O_5 facilities and striving to increase domestic cement production. This combination presents a situation favorable to exploiting phosphogypsum to help meet building material requirements. Table 2 shows the level of cement production in most of these countries and the rate at which cement production has increased over the past decade. Markets for phosphogypsum products can be expected to be particularly good in countries which are increasing cement production. For example, Indonesia has been importing substantial amounts of gypsum and therefore might consider whether an import substitution based on reprocessed phosphogypsum would be technically feasible and cost effective.

Examples of successful utilization of phosphogypsum in four countries are presented in following sections.

Table 1. Major Third World producers of phosphate rock and phosphoric acid

	Produces 100,000+ tons P_2O_5/year	Produces 100,000+ tons rock/year	Planning new P_2O_5 facilities	Planning new phosphate mining areas	Striving to increase cement production
Algeria		x	x		x
Brazil	x	x	x	x	x
China	x	x	x	x	x
Egypt			x	x	x
India	x		x		x
Indonesia	x		x		x
Jordan		x	x	x	x
Mexico	x			x	x
Morocco	x	x	x	x	x
Senegal		x	x	x	
Togo		x	x		
Tunisia	x	x	x	x	x
Turkey	x		x		x

Table 2. Cement production for major Third World producers of phosphate rock and phosphoric acid
(000 t)

	1971	1981	Average annual increase/decrease	Percent increase for 10 year period
Algeria	967	4,440	347	359%
Brazil	9,804	24,864	1,506	154%
Egypt	3,924	3,422	-50	-13%
India	14,928	20,772	584	39%
Jordan	419	960	54	129%
Mexico	7,524	17,844	10,320	137%
Morocco	1,481	3,606	212	143%
Senegal	241	372	14	60%
Tunisia	584	2,028	144	247%
Turkey	7,548	15,036	749	99%

FLY ASH/PHOSPHOGYPSUM CONCRETE MASONRY BLOCKS AS A CONSTRUCTION MATERIAL IN CHINA

China has a pressing need to construct large amounts of low-cost housing. China hopes to be able to provide each family with an apartment by the year 2000. This would require construction of 100 million square meters of housing annually. China has discovered fly-ash building blocks as a solution to the problem of disposing of fly-ash from blast and industrial furnaces, phosphogypsum and by-product lime from steel plants. Chinese officials have found the blocks are not only a sound usage for three industrial wastes but are technically superior and can be produced at a lower cost than conventional clay bricks. The newest development in utilization of fly-ash, phosphogypsum and by-product lime in China is the production of concrete panels. The momentum for using otherwise wasted phosphogypsum is thus well established.

JAPANESE DEVELOPMENTS IN PHOSPHATE FERTILIZER TECHNOLOGY WHICH PRODUCE HIGH-QUALITY BY-PRODUCT GYPSUM

Nissan has the best established technology for producing reusable gypsum. Nissan operates or has licensed 25 plants using the H-process. These are located in Japan, Australia, Ireland, France, Bangladesh, Belgium, India, Brazil, Morocco, the Netherlands, Taiwan, Turkey and Algeria. Three plants have been built by Nissan in Japan using the C-process and one plant is licensed in Indonesia. The total capacity of plants using the H-process is 8,090 tons per day. When the C-process plants are added to the total, the capacity for producing phosphoric acid fertilizer in the world using Nissan technology is nearly 9,000 tons (expressed as P_2O_5) per day. The equivalent yearly generation of phosphogypsum produced is more than 13 million tons. All of this gypsum can be recycled if the plants are properly operated.

THE DONAU CHEMIE PHOSPHOGYPSUM PROCESS WITH END USES IN BUILDING MATERIALS

At Pischelsdorf, about 50 km west of Vienna, Austria, Donau Chemie AG operates a 50,000 tons per year phosphoric acid plant using the Rhone-Poulenc dihydrate process. There is no convenient disposal area for the phosphogypsum and the plant was required to avoid environmental contamination. Therefore as early as 1970, Donau Chemie sought means for utilizing the large quantities of phosphogypsum which were being produced.

A marketing survey showed a demand for plaster in the building industry in Vienna and surroundings. Sufficient demand appeared to exist within a 250 km perimeter of the plant to absorb the output of a 150,000 ton per year gypsum processing plant. Marketing over a distance of more than 500 km was shown to be uneconomical due to high freight costs.

Donau Chemie purifies its phosphogypsum through a series of washing steps, to remove water-soluble impurities, and hydrocycloning, to remove fine particles. Recycling of water through a countercurrent washing system reduces the demand for fresh process water. The purified gypsum slurry passes to a rotary filter. The resultant filter cake is further dried in a centrifuge.

In 198l Donau Chemie completed construction of a new sulfuric acid plant beside the phosphoric acid plant. In such a sulfuric acid plant, huge amounts of waste heat are available. Using special Lurgi technology the waste heat was obtained at a temperature of 120° C. This was sufficient for concentrating the phosphoric acid produced up to 54% P205 in a single stage vacuum unit. Furthermore, the energy costs for drying and calcining the gypsum were reduced to one-third of the original costs.

The marketing of gypsum products at Donau Chemie became especially successful after the reduction of energy costs. Considering additional costs which would otherwise result from transport and safe disposal of the phosphogypsum, the profit gained by Donau Chemie is even greater.

Half of the gypsum production at Donau Chemie is sold as Plaster of Paris. Thirty per cent of the production is manufactured into gypsum partition panels. These panels are prepared by pouring plaster into moulds. The drying of the panels is also accomplished using waste heat from the sulphuric acid plant. The final twenty per cent of the production is marketed as joining plaster, mortar, and lime gauged gypsum plaster finish.

RECYCLING OF BY-PRODUCT GYPSUM VIA CHEMICAL CONVERSIONS: THE CHEMIE LINZ PROCESSES

In order to recycle phosphogypsum, Chemie Linz in Austria has adapted chemical conversion schemes which were originally developed for natural gypsum. The phosphogypsum may be either processed to cement and sulphuric acid or to ammonium sulphate. In addition, the HF and SiF_4 in the tail gases are converted to hydrofluorosilicic acid through scrubbing the effluent gases. Subsequently, aluminum fluoride is produced.

PHOSPHOGYPSUM IN BELGIUM:
THE CLASSIC PRAYON PROCESS AND THE NEW CENTRAL-PRAYON PROCESS

The classic Prayon process is one producing gypsum dihydrate which requires further cleaning. The dihydrate is purified using a process such as used by Donau Chemie, then dried and partially calcined to hemihydrate. The classic Prayon process has been in commercial use for more than 30 years. Improvements have been made during each decade including a better quality phosphoric acid product and effective utilization of lower grade phosphate rock as the raw material. The Central-Prayon process is carried out under an agreement between a Japanese firm, the Central Glass Company, and Societe Chimique Prayon-Rupel. The first commercial Central-Prayon process began production in 1965 in Belgium at the Engis plant of Societe Chimique Prayon-Rupel. The next plant was established by the Central Glass Company in 1967. In this process, the phosphoric acid plant produces gypsum in the hemihydrate state. Gypsum coming from the Central-Prayon process requires no further purification. After curing in free-standing piles to the dihydrate form, the phosphogypsum is screened and ground. The gypsum is then suitable for direct use in the plaster industry or as a cement retarder.

The Societe Chimique Prayon-Rupel has sold 102 plants world-wide using the Prayon dihydrate process and 11 plants using the Central-Prayon process. On a world-wide scale, about 33,500 tons of P_2O_5 per day are produced from plants using the Prayon dihydrate process. The Chemie Linz plant discussed earlier is a 60 ton P_2O_5 per day plant using the Prayon dihydrate process. Plants using the Central-Prayon process produce about 2300 tons of P_2O_5 per day.

"Utilization of gypsum from flue gas desulphurization processes and phosphoric acid production in the Federal Republic of Germany"

by H. J. PIETRZENIUK c/o Federal Environment Agency, Berlin

1. Summary

The increasing amounts of gypsum resulting from flue gas desulphurization in coal fired power stations, and phosphogypsum from phosphoric acid production represent a serious environmental problem, regardless of whether landfilled in dumped as solid form or discharged into surface waters. This contribution to the "2. International Symposium of Phosphogypsum" provides a brief survey of the amounts of calcium sulphate produced at present and projected amounts up to 1995 in the Federal Republic of Germany and of the possibility of utilizing it in different ways but primarily in the building industry.

The availability of natural gypsum in the FRG is restricting the utilization of by-product gypsum. Some effort has been made, however, to use gypsum from flue gas desulphurization.

2. Gypsum from Flue Gas Desulphurization

As a consequence of the Ordinance on Large Firing Installations, somewhat more than 1.75 million tons SO_2 will have to be precipitated annually in the Federal Republic of Germany (from 1995 onwards).

The market share of processes with gypsum as their end product presently amounts to approx. 90% which means that, after 1995, more than 2.4 million tons gypsum are likely to be supplied by coal-fired power station each year, plus another 1.0 million tons of gypsum annually by the brown coal power stations in the Rhine region. About two thirds of this volume, i.e. approx. 2.6 million tons per year, are supposed to be produced already in 1988.

The traditional gypsum industry presently supplies more than 2.7 million tons of gypsum for building plaster, sandwich-type plaster board and building elements per annum. Adding the import/export balance of some 0.5 million tons which plays a role especially for natural gypsum, one obtains a domestic production figure in this area of around 3.2 million tons per annum. These figures must be further increased by 1.4 million tons of natural gypsum and natural anhydrite per annum for the setting control of cements, as well as another 1 million tons of anhydrite contained in mining mortar. This translates into an overall volume of gypsum/anhydrite of 5.6 million tons per annum which is today almost exclusively produced by the German gypsum industry from natural sources.

The major part of natural gypsum undergoes certain pretreatment and, in most cases, is used as a building material for civil engineering purposes after the admixture of various additives. This area counts for 2.5 to 3.0 million tons per annum in the Federal Republic of Germany. The following uses are distinguished:

- plaster
- sandwich-type plaster board
- plaster slab partition walls
- plaster floor.

The traditional use of burnt gypsum is plaster. In most cases, plaster consists of so-called multiple-phase gypsum, i.e. mixtures of approx. 25 to 30% beta-hemihydrate (gypsum) and anhydrite.

DIN 1169 which constitutes the basis for the use of building gypsum is not limited to natural gypsum alone. If gypsum obtained from flue gas desulphurization plants meets the requirements of the standards, no distinction is made between products from natural gypsum and gypsum from desulphurization plants.

The amount of harmful trace elements which might preclude the use of desulphurization gypsum for interior purposes falls within the range of natural gypsum. This also applies to its radioactivity so that there are no objections against the use of desulphurization gypsum as building material. The German gypsum industry has formulated the following additional requirements which desulphurization gypsum must meet:

Humidity	10%
$CaSO_4\ 2H_2O$	95%
MgO	less than or equal to 0.10%
Chloride	less than or equal to 0.01%

Sulphite	less than or equal to 0.25%
pH	5 - 9
Organic constituents	less than or equal to 0.10%
Color	white
Smell	neutral

Most of these requirements are met by the processes offered, special treatment may be required in some cases. The scope of such processing depends on the crystalline form. Sufficient residence times of the gypsum crystals at low rates of gypsum oversaturation permit the production of the desired coarse-grained gypsum in the absorber; such coarse-grained gypsum is much easier to dehydrate than gypsum having needle-shaped crystals. For other processing stages, too, the use of gypsum having a coarse-grained structure is more favourable. The gypsum so prepared is partly calcined at temperature's of around 140 °C in a calcining furnace. The end product is beta-hemihydrate or plaster.

Another way is to mix gypsum from flue gas desulphurization (FGD) plants with anhydrite obtained from the production of hydrofluoric acid (such anhydrite serving as bonding agent) and to use this mixture in the production of floor pavement substance. Given an area of 40 to 50 million square meters of floor pavement completed annually in the Federal Republic of Germany, and further given a substitution rate of 50% by the above-described new building material, one obtains an annual demand of some 2 million tons. This figure contains 600,000 to 1 million tons desulphurization gypsum. Such a volume could be marketed additionally without displacing natural gypsum which is primarily used for the production of plaster and sandwich-type plaster board. Such a substitution would primarily affect the market for cement which is produced at high energy input rates and continually rising costs.

Before grinding the cement, gypsum and anhydrite are added to the burnt cement clinker for setting control purposes. According to DIN 1164, the calcium sulphate content of Portland cement is limited to a maximum of 3% SO3. Relating to gypsum, this translates into a realistic demand in the order of 5% which is presently covered almost exclusively by natural gypsum and anhydrite. Requirements concerning the chemical purity of gypsum used in the cement industry have as yet been formulated only as far as DIN 1164 sets forth that the permissible limit percentages of CO_2, MgO, SO_3, Cl in the cement must not be exceeded. As a maximum of 5% desulphurization gypsum is added, these values are easily adhered to without the need for additional purification processes.

Given a future annual demand for approx. 1.4 million tons of natural gypsum and anhydrite, a realistic figure would be 500,000 to 600,000 tons of desulphurization gypsum per annum as a substitute.

Further development work in the field of a utilization of gypsum from flue gas desulphurization aims at producing from flue gas gypsum - obtained in the form of beta-dihydate - the more stable alpha-modification.

Uses in coal mining are particularly obvious because of its good early and final strength.

First tests in underground workings have underpinned the suitability of mining mortar made from desulphurization gypsum. Owing to its improved filling rate and a more favcurable setting temperature, such a mining mortar is probably superior to conventional mining mortars, especially if it is produced directly in connection with a flue gas desulphurization plant. The demand for mining mortar in the Federal Republic of Germany is in the order of 1.3 million tons per annum, and the trend is increasing. Careful estimates indicate sales of desulphurization gypsum between 600,000 and 700,000 tons per annum.

Another completely new use of gypsum which is becoming more and more important against the background of the present known to have chemical impurities which greatly affect its setting and cristallization properties and often results in deterioration of the bulk properties of the gypsum products.

The major problems preventing its use at present are chemical impurities specific to phosphogypsum and the Ra 226 presence. Because of the alternatives available, i.e. FGD-Gypsum and gypsum from natural resources, there is no chance at present that significant quantities of phosphogypsum can be used in conventional gypsum products in the FRG. At present there are four companies producing wet phosphoric acid. Only in one company (VEBA-Chemie AG, Embsen) relatively small quantities of about 90 - 600.000 t/a phosphogypsum are used for the manufacture of gypsum-plasterboard. About 700.000 t/a phosphogypsum are dumped on land or - in one case - into a river.

Phosphogypsum - An Overview

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Introduction

Phosphogypsum is a by-product of the manufacture of phosphoric acid from phosphate rock by the wet process.* The overall reaction is as follows:

$$Ca_{10}(PO_4)_6F_2 + 10\ H_2SO_4 + 20\ H_2O \text{------} 10\ CaSO_4\ 2\ H_2O$$

$$+ 6\ H_3PO_4 + 2HF$$

Each ton of P_2O_5 in the acid is associated with the production of 4.5 to 5.5 tons of phosphogypsum. In other words, for every ton of phosphate rock about 1.5 tons of phosphogypsum are formed. The exact quantity depends on the phosphate rock quality.

Figure 1 shows, in schematic form, estimated and projected worldwide production of P_2O_5 and phosphogypsum for the period 1970-2000. As of 1983 some 120-150 million metric tons (mmt) of phosphogypsm were being produced annually. If historic trends continue, 150-200 mmt of phosphogypsum will be produced annually by 1990, increasing to 220-280 mmt by 2000.

Impurities in the Phosphogypsum

The phosphogypsum as it comes from the phosphoric acid plant may contain a number of undesirable impurities, especially phosphates and fluorides. Typical levels of impurity for dihydrate processes are:

Phosphoric acid content, as P_2O_5 = 0.66%

Fluoride content, as CaF_2= 1.44%

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* The terms phosphogypsum and by-product gypsum are used interchangeably in the technical literature. Waste gypsum is also a synonym sometimes, but more often describes phosphogypsum which has been dumped or otherwise discarded.

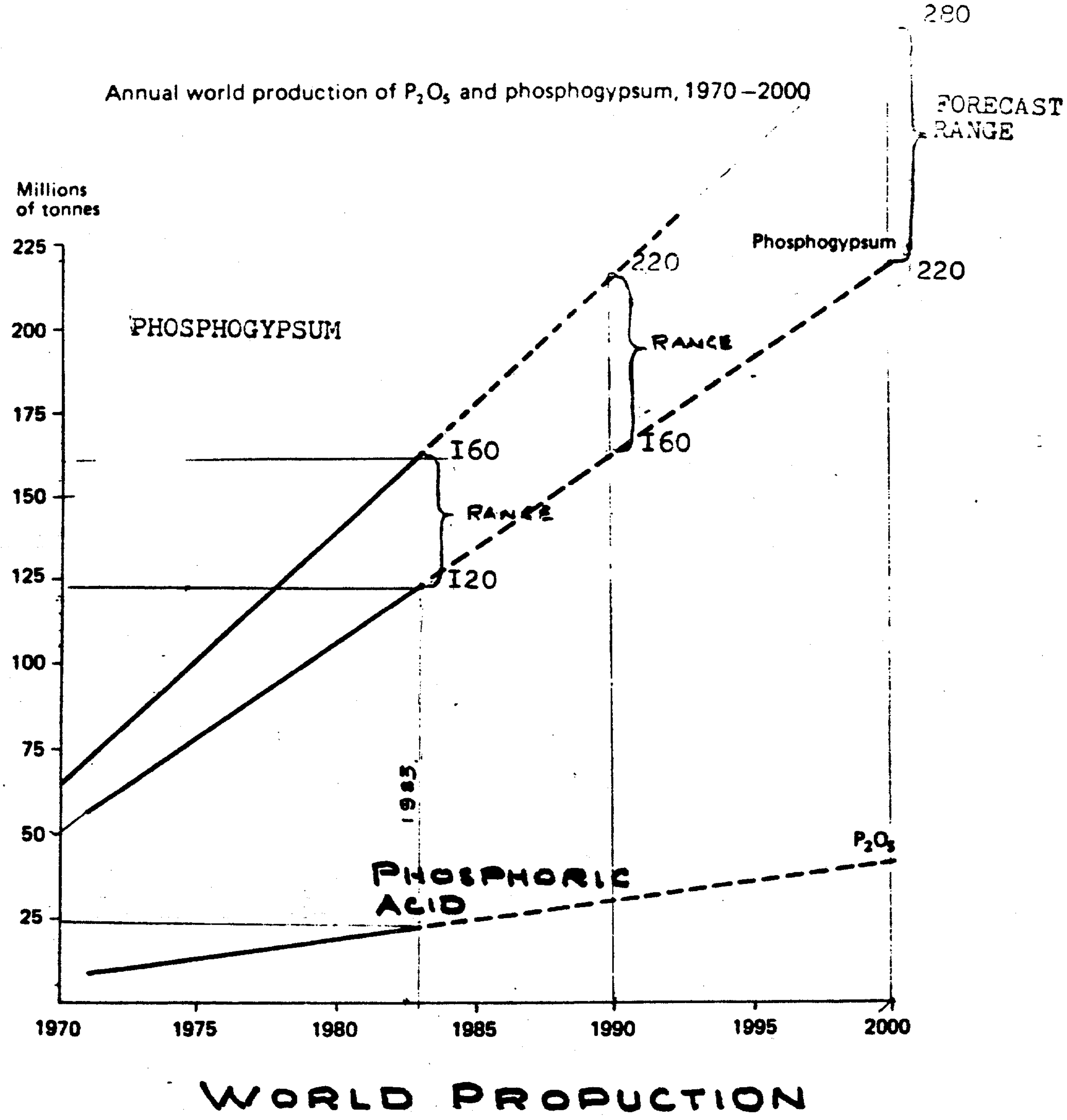
Annual world production of P_2O_5 and phosphogypsum, 1970 – 2000
Millions of tonnes
225
200
175
150
125
100
75
50
25
1970
1975
1980
1985
1990
1995
2000
PHOSPHOGYPSUM
Phosphogypsum
280
FORECAST RANGE
220
220
160
160
120
RANGE
RANGE
1985
PHOSPHORIC ACID
P_2O_5
WORLD PRODUCTION

Figure 1

The quantity of impurities in the phosphogypsum depends primarily on the phosphoric acid process used, on the operation of the plant, and on the quality of the phosphate rock,

Background and History

The E.E.C. is keen to encourage the reduction of pollution and the recycling of wastes and prefers to refer to wastes as "Secondary Raw Materials".

The E.E.C. published an overview of the situation in March 1984, "Ten Years Of Community Environment Policy". This traced the actions and activities since 1972. Action was taken in 1972 because:

a. Environmental pollution and nuisances do not stop at frontiers.

b. Major differences in environmental policy could easily lead to distortions of competition.

c. The health of natural life-support systems had to be assured to the basis for further economic and social advances.

d. It was politically unacceptable that very different living conditions should develop in different member states.

The main principles of community environment policy were laid out in the First Action Programme of 1973.

The primary objectives of community environment policy were also spelled out in the First Action Programmes.

The three broad categories of action have been

- To Reduce and Prevent Pollution and Nuisances
- To Improve The Environment and the Quality of Life
- Community Action (or where applicable, common action by member states) in international organizations dealing with the environment

Waste Management

The community overall objectives in the field of waste management have been threefold:

i. To reduce the quantity of un-recoverable waste
ii. To recycle and reuse waste to the maximum extent for raw materials and energy

iii. to dispose safely of any remaining non-recoverable wastes

Directives were issued in 1975 and 1978 requiring member states to designate competent Authorities for waste disposal requiring them to take appropriate steps to encourage: prevention, recycling, processing and re-use of waste, and the extraction of raw materials and energy thereform.

Toxic and dangerous wastes were listed in 1978 and the main substance affecting phosphogypsum was the inclusion of cadmium in the list.

Cadmium was further controlled by E.E.C. Directive 83/813 and 85/53 and the producers given to 1st January 1986 to conform to either:

- Limit values
- Quality objectives

N. B. manufacture of phosphoric acid and fertiliser has temporarily been excluded.

The E.E.C. technocrats have been striving for a long time to get phosphogypsum included as a pollutant and worthy of control but their attempts have been thwarted by the strength of the political lobby mounted by the phosphoric acid producers.

The E.E.C. policies have been based on the philosophy that:

- "Prevention Is Better Than Cure"
- "Action at Appropriate Level"
- "The Pollutor Pays"

To achieve this the E.E.C. encourages

- Cleaner technologies
- Alternative routes for manufacture
- Beneficiation at source
- Transfer of technologies where appropriate
- The reduction and abolition of non-recoverable waste
- The recovery, recycling and re-use of waste for raw materials and energy
- The proper management of non-recoverable waste

Action Programme of the E.E.C. on Environment

Resolutions of council were passed in 1983 outlining the continuation and implementation of E.E.C. policies and action programme which includes:

- Integration of the environmental dimension into other policies

- Environmental impact assessment (E.I.A.) procedure

- Reduction of pollution and nuisance
    - Atmospheric pollution
    - Fresh water and marine pollution
    - Trans frontier pollution
- Dangerous chemicals
- Waste management in particular toxic and dangerous wastes
- Encouraging the development of clean technologies
- Co-operation with developing countries

Research and Development

The E.E.C. programme for R & D includes significant funding for:

E.E.C./234/86 Directive in environment

E.E.C./235-86 Directive on primary and secondary materials

Note: The E.E.C. prefers to refer to secondary raw materials and not waste

Market and Plant Capacity

It has been estimated that the world production of PG is 120,000,000 tons per annum and the european element is 12,000,000 tons.

There has been a cut back in Europe due to the recession. This amount fluctuates but the overall trend is for substantial increase in growth and by the year 2000 projected amount is 220,000 throughout the world to cope with agricultural demands to feed the expanding populations.

Competitors

The major consideration in marketing products made from PG is the cost of the purification involved to remove impurities.

In many instances the cost of purification is more than the cost of natural gypsum mined locally and adjacent to the user.

Generally only in countries where there is no natural gypsum or the cost of transport is prohibitive can PG compete economically.

Desulphurisation

The awareness of the harm created by Acid emissions from power stations and acid rain means that there will be an availability of relatively pure gypsums precipitated by desulphurisation installations.

This will seriously affect any proposals to purify and market phosphogypsum.

Inputs and Raw Materials

The source of the parent rock plays an important role in the amounts of impurity present in the PG ad it has been concluded that the rock from igneous rocks is relatively much purer than that from sedimentary rocks.

Resource Conservation

The recycling of wastes will preserve dwindling stocks of primary materials we are squandering valuable materials by dumping waste.

Beneficiation at Source

There is a growing tendency to beneficiate at source of the parent rock and transport either upgraded material even phosphoric acid.

Transfer of Technologies

Cleaner technologies in the manufacture of phosphoric acid have been advocated and new processes have been evolved. These can be installed nearer the source of the rock and it will be necessary to transfer some of the new technologies to the under developed countries which have the deposits of the raw materials. existing producers will be reluctant to transfer their secret to politically and financially unstable under developed countries.

Clean Technologies

. Incentives and Assistance in Implementation of Innovative Technologies
. More Efficient Production
. Less and Purer By-Products
. Higher Grade Acids
. Utilisation of Lower Grade Raw Materials for Fertilisers

Exploration and Exploitation

. Alternative sources of Raw Materials in the Developing Countries.

Resource Source

The fact remains that PG is a valuable source of resource and should not be indiscriminately discharged or disgarded.

Phosphogypsum is a very valuable source of mineral resource with particular reference to calcium and sulphur. ($CaSO_4$ $2H_2O$)

It also contains useful recoverable amounts of

- Fluorine
- Cadmium
- Phosphate
- Radioactivity

Locations

This is not a lesson on geography, but a brief review of the geographical implications which may be of interest to you.

The majority of the considerations made to date refer to the European Community area and the state of the art in the Eastern Block in Europe has not been affectively studied or investigated. The recent inclusion of Portugal, Spain and Greece would deserve further consideration in the E.E.C. area. Austria, Switzerland, Scandanavia have not been considered.

The main considerations have been of the discharge of phosphogypsum into the aquatic environment and land fill sites.

Black Sea

No information has been available for discharge into the Black Sea.

The Mediterranean is an open cess pit and any of us who have lived on the exotic shores of Tripoli are aware of the daily attention to the broadcast bulletins to tell you which beach is safe for swimming in order to avoid severe bacteriologically carried infections.

The Adriatic is equally heavily polluted.

The Baltic Sea has been subject in the past to receiving massive doses of pollution in the form of industrial wastes, but the discharge of materials such as PG has been severely restricted especially in Finland, Sweden, Poland and Denmark.

The North Sea receives the wastes from the Mighty Rivers Elbe, Rhine, Seine, Thames, Humber and Forth and there are phosphoric acid plants disgorging their wastes freely into the sea. The French fishermen at le Havre have continually protested about the yellow muds and have forced the producers to dump by barge 15 KM into the English Channel.

The Irish Sea receives PG from Belfast, Whitehaven and Avonmouth and it is reputed to be the most Radio-Active polluted sea in the world.

The pollution is not only the result of Windscale/Selafield and the PG contributes a small but nevertheless significant amount of radioactivity.

Note: Environmental considerations are as important as profit making. Volatisation by calcination of cadmium and organics at source will be more important in the future.

Process and Engineering Technologies

I have listed over 70 different potential uses of PG in my report to the E.E.C. The technologies have been Well documented previously, many by some of you present today and I do not propose to discuss these in detail.

Each individual use could be the subject of lengthy and detailed further R & D and the assembled scientific and technical expertise is entirely capable of any such elaboration, study and investigation.

Any interference by me would only be impertinance to such a learned and professional assembly and would be what we in Ireland refer to as "Teaching Our Grannies How To Suck Eggs". Sufficient is to briefly mention a few items which may be of mutual interest.

Bacteriological Treatment

1. The use of biotechnology to treat a combination of sewage and PG to produce hydrogen sulphide which can be scrubbed and used for further production of sulphuric acid or elemental sulphur.

This was demonstrated many years ago at London County Council and the National Physical Laboratory at Teddington but further study is necessary.

The technology could be revived and I am trying to get the authorities in Northern Ireland to back a scheme at Belfast Lough where 75,000 tons of PG are dumped each year into Belfast Lough and every night a ship the Divis takes 1,000 tons of untreated sewage and dumps it in the sea off Whitehead where I live.

Needless to say all the sulfuric acid used in Ireland is from imported sulphur at a high cost due to the cartel control of sulphur.

Soil Conditioners

2. The use of PG as a soil conditioner and pelletising this with other organic and mineral wastes to provide a more acceptable form of handling has indeed potential and I have successfully carried out tests in Germany using diverse materials such as: cement flue dust, dolomite waste, basalt meal, P.F.A., spent mushroom compost, organic wastes, forest bark etc. and made very good pellets which can be used as low grade fertilisers or soil conditioners. Mineral additives can. be used to eradicate, such problems as hypomagnasaemia in cattle.

Fluidised Bed: Sulphur/Lime

3. Twin Kiln Working On a Fluidised Bed Principle: I have been involved in the preliminary designs of a special kiln and I have been trying to get the E.E.C. to fund a research project on this subject.

4. Alpha Hemi-Hydrate as Opposed to Beta Hemi-Hydrate: This subject has been well tried and proven in Europe and we have the I.C.I. process which is currently marketed by Saltzgitter and the Guilini process which is engineered by Babcock Deutche can be available. There are advantages and disadvantages of these processes.

5. Waterproof Phosphogypsum: This. has been under study I understand in Germany and Russia and successful break through on waterproofing would be a major step forward especially to those of us destined to live in moist climates.,

6. Gypsum Fibre Boards: There has been a marked growth in the marketing of G.F.B. especially in Germany where the Simplekamp process (marketed by Saltzgitter) is successfully replacing the conventional double sided cardboard coated plaster board.

The integral mixture of waste paper and gypsum assists in the disposal of industrial waste and municipal wastes.

7. The use of PG as a medium for building boards was the subject of a vigorous campaign in London a few years ago where the natural gypsum producers persuaded London County Council that the radon element was harmful to the inhabitants of buildings constructed by phosphogypsum material. C .F. "The Enemy Within".

8. Asbestos Substitute: The possibility of the manufacture of whisker fibres to be used as a substitute for asbestos for insulation and lagging presents a good opportunity for the utilisation of the PG. These could be combined with Perlite to make structures for space travel.

9. Lightweight Aggregate and Elements: This has many applications throughout the construction industry. A new type of machine for foaming gypsum products is being evolved. C.F. Aercrete".

10. Solvent Extraction:

- Uranium
- Cadmium

11. Nutrient Blocks: E.E.C. R & D : I have made current applications into the E.E.C. for funding the manufacture of nutrient/therapeutic blocks for animal and fish feeds and for pellets for soil conditioners under the E.E.C. Action Programme on Research of Primary and Secondary Materials E.E.C. 235/86.

The Aims and Principles of Community Environment Policy

The main principles of the community's environment policy were already set out in the First Action Programme of 1973. They include the following:

i) the best environment policy consists in preventing the creation of pollution or nuisances at source rather than subsequently trying to counteract their effects;

ii) environment policy can and must be made compatible with economic and social development;

iii) effects on the environment should be taken into account at the earliest possible stage in all technical planning and decision-making processes;

iv) significant damage to ecological balance must be avoided;

V) standards of scientific and technological knowledge should be improved: relevant research should therefore be encouraged;

vi) the cost of preventing and eliminating nuisances must in principle be borne by the polluter;

vii) care should be taken to ensure that activities carried out in one state do not cause any degradation of the environment in another state;

viii) the community and its member states must take account in their environment policy of the interests of the developing countries;

ix) the community and the member states must make their voices heard in international organizations dealing with aspects of the environment;

x) the protection of the environment is a matter for all in the community, who should therefore be made aware of its importance;

xi) actions should be taken at the level appropriate in relation to the type of pollution concerned;

xii) major aspects of environment policy in individual countries must no longer be planned and implemented in isolation;

xiii) community environment policy should aim, as far as possible, at the coordinated and harmonised progress of national policies, without, however, hampering progress at the national level. But, the latter should be carried out in such a way that it does not jeopardise the satisfactory operation of the common market.

Objectives

The primary objectives of community environment policy were also spelled out in the First Action Programme, It should:

i) prevent, reduce and as far as possible eliminate pollution and nuisances;

ii) maintain a satisfactory ecological balance and ensure the protection of the protection of the biosphere;

iii) ensure the sound management of and avoid any exploitation of resources or of nature which cause significant damage to the ecological balance;

iv) guide development in accordance with quality requirements especially by improving working conditions and settings of life;

V) ensure that more account is taken of environmental aspects in town planning and land use;

vi) seek common solutions to environment problems with States outside the community, particularly in international organisations.

In order to translate these principles and objectives into practice, implementation of the Community's Environmental Action Programmes has been within three broad categories of action:

- to reduce and prevent pollution and nuisances;
- to improve the environment and the quality of life;
- community action (or where applicable, common action by the member states) in international organizations dealing with the environment.

Organization

A major issue in Europe is the inconsistency throughout the member states of the levels of pollution and contamination of the

Atmosphere
Land
Water

The lack of mutually accepted policies extends to

Standards
Nomenclature
Units

Legislations differ in each member state and control systems are at variance.

It has been recommended that Europe considers a Centralised Environment Protection Authority similar to that in America E.P.A.

This may be a two-edged sword and would be very difficult to implement and administer in Europe.

Education and Training

The E.E.C. recommend education and training at all levels.

For R & D they fund individuals, organizations and research establishments in innovation technologies regarding disposal and recycling of waste.

Also funding is available for demonstration projects which provide the link between R & D and commercially viable projects.

Phosphogypsum has recently been included in the funding proposals.

Planning and Programming

The action programmes on environmental protection play an important part in the promotion of schemes to improve the quality of the environment and the current programme 1982-86 will be extended to 1990.

The implementation of environment impact assessment is expected to be legalised by June 1988.

Finance

It is all very well for administrators and technocrats to glibly come to the conclusion:

The Pollutor Pays

While pollution is abhorred, the cost of cleaner technologies will eventually be reflected in the cost of fertilisers across the farm gate.

The producers have to exist and make profits and are generally not subsidised by governments, nor are they charitable institutions.

The funding of R & D projects and also demonstration projects is a step in the right direction.

The producers will request compensation for any innovation required and sympathetic hearing should be given.

Economics

While we have considered the aspects of environment, ecology, energy there is the vital aspect of the cost of any improvement or cleaner technologies to be introduced: in other words: Economics

The producers all cry poverty and hold the threat that any punitive legislation would lead to the closure of the chemical plants and resultant unemployment.

Suggestions have been made that there should be some sort of financial incentive to the producers to enable them to effectively introduce innovations.

This could be achieved by cash advances, loans, grants, tax, holidays, etc.

It is concluded that the producers are unlikely to introduce change unless forced to do so by new legislations, or by substantial incentives.

The introduction of punitive measures will be very difficult to enforce and monitor. However the Germans seem to have effectively brought in measures to ensure that the pollution is reduced to the minimum, but there are always unforeseen accidents as we have all witnessed recently by the phosphate chemical discharge into the Rhine at Basle in Switzerland.

Cost benefit analysis should review that the recycling of PG will in many instances lead to significant import substitutions, overall direct or indirect energy savings and an element of employment creation coupled with overall conservation or primary and secondary natural resources.

It is necessary to assess the economic implications of environmental strategy and management.

Environmental impact assessment will affect all our future deliberations, decisions and policies.

Conclusion

This has been an overview of the position as regards the situation of phosphogypsum in Europe.

It is plainly clear that the problems involved are world-wide in both developed and under developed countries and that all parties concerned share a common interest in finding practical, realistic and economic solutions to the problems involved.

I feel confident that there is every chance of achieving these goals and we have to find equitable solutions between conservation vs.. development and protection vs. production and/or improvement, environment, ecology and economics.

The standard of the papers presented here are a clear indication that everyone present is keen to ensure that our environment will be a cleaner, safer and a better place to live in for our children and there will be increased efficiencies in our industries.

We must act now to preserve our dwindling natural and mineral resources and this includes the

- Conversion and Recovery
- Recycling
- Re-Use
- Reduction of PG Amounts and Pollution

of phosphogypsum throughout the world.

UTILIZATION OF PHOSPHOGYPSUM: STRUCTURE AND ACHIEVEMENTS OF A COOPERATIVE RESEARCH PROGRAMME

J J MALAN

COORDINATOR: NATIONAL RESEARCH PROGRAMME FOR WASTE MANAGEMENT
FOUNDATION FOR RESEARCH DEVELOPMENT
COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH

ABSTRACT

A cooperative research programme at the Foundation for Research Development (FRD) of the Council for Scientific and Industrial Research (CSIR) of South Africa looks at various aspects of Waste Management. Due to various inputs research on the utilization of phosphogypsum has been done on a wide variety of aspects.

Phosphogypsum is produced at different fertilizer plants spread over the country. Not all of these plants are accessible to the main marketing areas and therefore has to utilize its phosphogypsum locally, Development work on the utilization of phosphogypsum includes research into the use as building blocks: plasterboard; cement retarder in cement production and as a soil ameliorant. Furthermore aspects related to both sea and land disposal were al so investigated. Research on sea disposal resulted into the construction of a sea pipeline that disposes of phosphogypsum and other effluents at sea. Research on land disposal indicated that soil structures could suffer from chemical attack.

The most promising use of phosphogypsum in South Africa is as a soil ameliorant to counteract soil acidity. This research is in step with research internationally and it can lead to greater usage of phosphogypsum in South Africa in the near future.

INTRODUCTION

The Foundation for Research Development forms one of the many activities of the Council for Scientific and Industrial Research of South Africa. The Foundation funds and coordinates research in many fields, one being waste management. The National Research Programme for Waste Management consists of four subprogrammes, of which one addresses the various aspects of chemical waste management. This is structured under topics such as disposal, leachate control, co-disposal and utilization. The programme cooperates with a well-identified community that interacts by assisting in identifying research needs and in evaluating the progress in current research projects. The programme functions countrywide and is multidisciplinary by nature. It is a cooperative programme thus projects are co-funded, co-managed and a strong interaction between the private and public sectors is established. In the programme's function research needs are addressed with the ultimate goal of technology transfer. To achieve this, centres of expertise are established.

ORIGIN AND COMPOSITION OF SOUTH AFRICAN PHOSPHOGYPSUM

Phosphogypsum originates from six different plants situated mainly in the centre and eastern sectors of the country. The positioning of these plants with reference to existing railway links, the natural gypsum sources and the marketing centres are shown in <u>Figure 1</u>. Only three of the plants are within reach of the major industrialized sectors and therefore near the markets. This is a very important aspect since the viability of any utilization venture can hinge on the transport costs. Because of this, efforts are being made to utilize the phosphogypsum locally as far as possible.

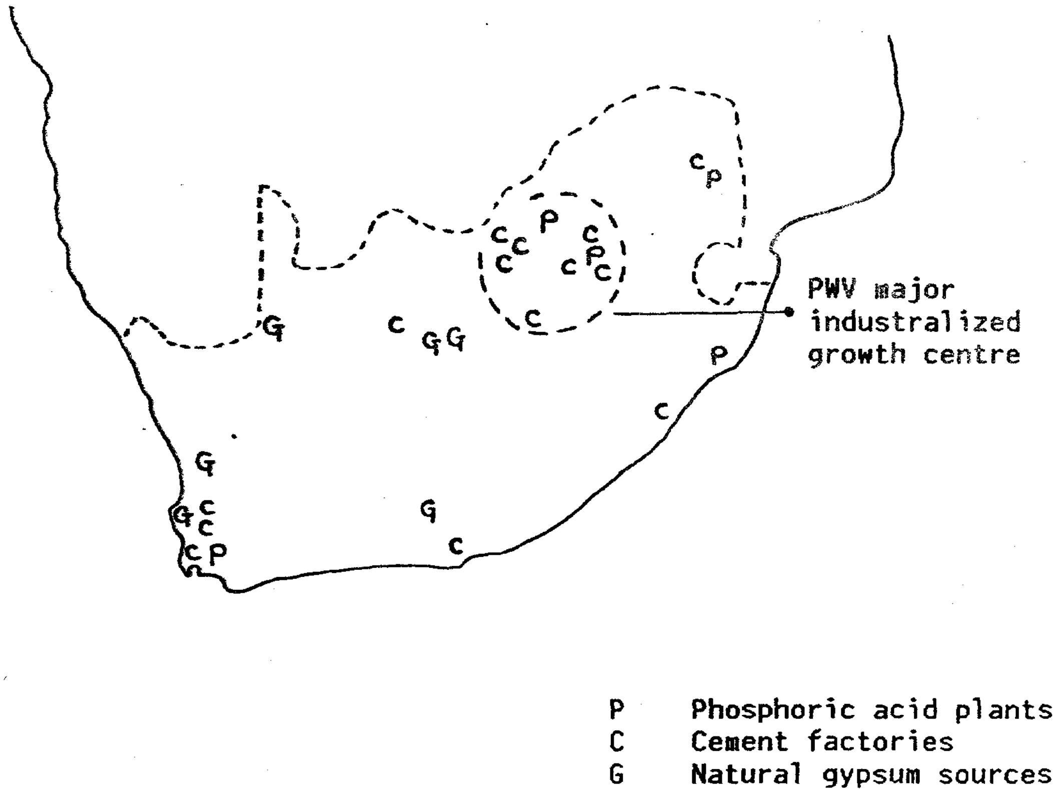

Figure 1. Map indicating location of phosphoric acid plants, cement factories and natural gypsum deposits

The total amount of phosphogypsum generated annually is between three and five million tonnes with the bulk being produced by the three major plants. Since the basic feedstock for the plants originates from the same source, that is the Palabora phosphate rock, the composition of the phosphogypsum except for process characteristics changing it here and there, is more or less the same for all six plants.

The production rate of the six plants are given in TABLE I.

TABLE I. PRODUCTION RATE OF PHOSPHOGYPSUM AT THE DIFFERENT PLANTS IN SOUTH AFRICA (ACCORDING TO KRüGER)

Plant	Approximate annual production (kilotons)	Approximate accumulated quantity (kilotons)
Fedmis (Pty) Ltd Phalaborwa	(i) Hemihydrate: 330 (ii) Gypsum : 700	7 000 of hemihydrate and gypsum together
Omnia Phosphates (Pty) Ltd Rustenburg	Gypsum : 150	500
Kynoch (Pty) Ltd Chloorkop	200	1 500
Triomf Fertilizer (Pty) Ltd Potchefstroom	290	2 500
Triomf Fertilizer (Pty) Ltd Richards Bay	1 560	5 000
Triomf Fertilizer (Pty) Ltd Somerset West	70	200
TOTAL	3 300	16 700

With reference to the map in Figure 1, the Kynoch, Omnia and Potchefstroom plants are nearest to the major markets and are therefore utilized the most. The Somerset West plant is small and a port ion of the phosphogypsum produced here is used in vineyards. The Fedmis plant utilizes some of the hemihydrate it produces for cement production; the rest is stockpiled. Disposal on land at the Richards Bay plant was planned to be substituted by a sea disposal operation. However, although the plant is being moth-balled and this development might not be utilized for phosphogypsum for some time, the study was completed.

In a survey done a few years ago one of the largest dumps was sampled intensively on three levels for chemical analyses and the results indicated a composition of 96% $CaSO_4.2H_2O$, 2% P_2O_5 and 0,5% F, with trace elements and rare earths making up the rest and being close to background values. The total analyses are given in TABLE II.

TABLE II. CHEMICAL ANALYSES OF A TYPICAL SOUTH AFRICAN PHOSPHOGYPSUM (ACCORDING TO KRUGER)

COMPONENTS	CONCENTRATION
Main Components	%
MnO	0,02
CaO	33,1
K_2O	< 0,01
Cl	0,03
SO_3	42,4
P_2O_5	2,14
SiO_2	0,91
MgO	0,29
LOI	20,26
% Acid	0,48
Total %F	0,58
%Sr	0,23
Trace Elements	ppm
Water sol F	9
Water sol P	0,5
Y	50
Zr	185
Cu	103
Ba	140
Zn	6
Ni	13
Hg	< 50 ppb
Particle size	% Distribution
> 350	0,9
> 250	1,8
> 150	12,1
> 75	34,6
> 53	15,0
> 20	19,8
< 20	18,3
% LOD	26,4
pH	7,1

PROJECTS

Research done in the country. on the utilization and disposal of phosphogypsum includes work on building blocks, plasterboard, cement retarder, cement production, soil amelioration, pollution impacts and sea disposal .

The strength and solubility characteristics of phosphogypsum blocks as a building material was investigated by the CSIR on contract for industry. The results proved that the material could be used for either inner walls or for exterior walls if a large roof overhang is provided. The economy of this, however, was not favourable and it was therefore not implemented.

Investigations on plasterboard manufacture was done by industry itself and mainly focussed on means to purify the phosphogypsum at low cost. This resulted in a preprocessing plant that purifies the material for the manufacture of plasterboard and related products.

The use of phosphogypsum as a cement retarder was investigated by the cement industry, In this investigation it was found that apart from the physical characteristics of the phosphogypsum that caused problems in the handling thereof, it also led to erratic setting times of the cement. Apparently some of these problems have been solved and phosphogypsum might, depending on the economic viability factors, be utilized as a retarder in future.

Work done on the use of phosphogypsum for the production of cement resulted in at least one plant in the country producing cement from dihydrate phosphogypsum. Although this is done on an economically feasible basis it is not likely that any more plants will come into being in the near future.

The application of phosphogypsum as a soil ameliorant is one of the projects that shows potential for future utilization. Some agricultural areas have highly leached sandy soils, which due to aluminum toxicity, cause low yields. Studies in the application of phosphogypsum to counteract this negative feature proved to be very effective for some crops. Crops that seem to benefit from the application are maize, lucerne , and to some extent sugar cane. Trials are also currently being conducted on avocados, tobacco and others. The most spectacular results were, however, achieved on maize and lucerne. Particularly on maize the root development showed a significant improvement with phosphogypsum treatment. Studies on the migration rate of phosphogypsum through the soil also indicated that it was much faster than expected. The net effect of this is a total ameliorative action in the root zone due to neutralization, a self-liming effect and an increase in the Ca to Al ratio in the soil. This effect is illustrated in Figure 2 as observed in a pot trial.

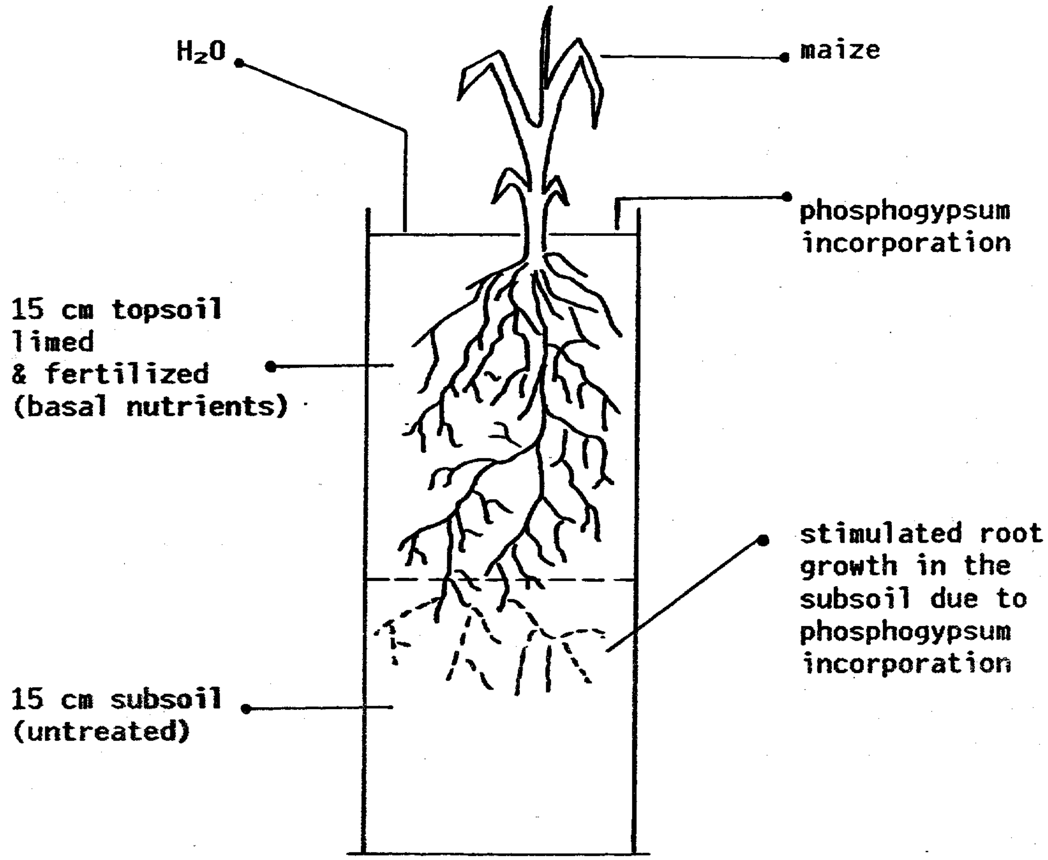

Figure 2. **Amelioration effect in subsoil by phosphogypsum (according to Fey)**

The impact of phosphogypsum and its effluent on soil structures is a real problem since some of these dumps can be situated on sensitive aquifers. Investigations done indicate that soils can be subjected to acid attack by this effluent resulting in the formation of soluble products which could lead to increase in the permeability of the soil structure.

The construction of a phosphoric acid plant producing, under optimum conditions, a total amount of 6 000 tonne phosphogypsum per day on the north-eastern coast of South Africa led to the investigations into sea disposal. This was conducted under the auspices of the South African National Committee for Oceanography Research (SANCOR). In spite of the relative short time allowed for this study every attempt has been made to develop a pipeline facility, which is large by any standard, in the best possible way. Throughout the project the best available scientific information has been utilized and the design, planning , construction and operation of this facility have been dictated by environmental requirements or criteria. The location of the pipeline relative to both the harbour and sanctuary as well as the seabed topography are illustrated in Figure 3.

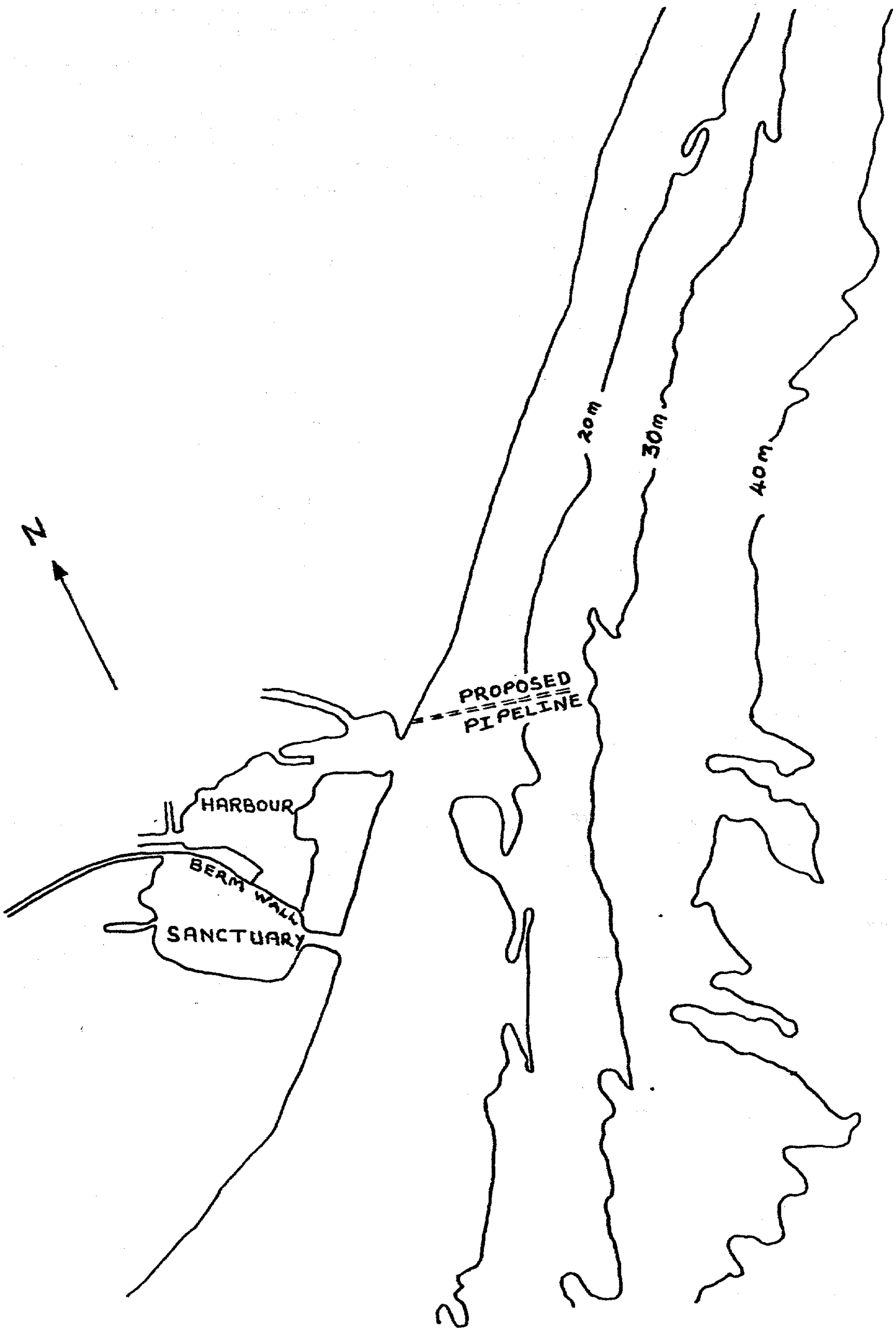

Figure 3. Location of the phosphogypsum pipeline relative to both the harbour and sanctuary as well as the seabed topography (according to Lord)

The data on the pipeline are summarized in TABLE III. This describes the pipeline to be 4 km long with a diameter of 1, 2 m. Ejecting phosphogypsum from sixteen points at a velocity of 15 m/s at a depth of 25 m under the sea surface. The height of the trajectory of the phosphogypsum is by design 15 m above the seabed allowing a contact period of 25 minutes between the particles and water thus achieving a 95% dissolution. It is estimated that in the end 4 km^2 of the seabed will eventually be covered by phosphogypsum.

TABLE III. DATA OF THE RICHARDS BAY PIPELINE (ACCORDING TO LORD)

Total length	4 km
Diameter	1,2 m
Wall thickness	12 mm
Density of slurry	0,93 g/cm^3
Temperature at outlet	45 °C
Velocity	15 m/s
Ejection points	16
Depth	25 m
Height of trajectory	15 m
Period of particle contact with water column	25 min
Percentage of phosphogypsum dissolved	95%
Estimated area of seabed to be covered	4 km^2

The accumulated amount of phosphogypsum produced in the country is estimated at 15 million tonnes. With an annual production rate of between 3 and 5 million tonnes depending on both the economy and the demand through farming activities. Annually this stream of phosphogypsum is either disposed at sea or on land or utilized in cement production, as a soil conditioner or to produce gypsum products. This is summarized in TABLE IV indicating the relative kilotonnes and percentages.

TABLE IV. BREAKDOWN OF THE AMOUNTS OF PHOSPHOGYPSUM UTILIZED AND DISPOSED OF PER ANNUM (ACCORDING TO KRüGER)

Operation	(kilotonnes/annum)	Percentage
Cement production	130	4
Soil conditioner	100	3
Gypsum product	30	1
Sea disposal	1 500	45
Land disposal	1 540	47
	3 300	100

CONCLUSION

The above indicates that utilization of phosphogypsum is not very well developed in the Republic of South Africa. The main reason for this is the total dependence of each venture on the economic viability thereof. At the moment the use that shows the greatest potential is as a soil ameliorant provided that it can be proved that there will be no detrimental effects on the soil in the longterm and that the concept can be successfully marketed to the farmer. It is, however, also envisaged that other uses could develop with time, depending on the right stimulus being either technical or economical.

REFERENCES

Fey, M.V. and S.M. BUYEYE. 1985. Maize growth and acid soil responses to treatment with gypsum and lime (unpublished article). University of Natal, Pietermaritzburg.

Krüger, J.E. 1980. Report on a preliminary technical feasibility study into the disposal, storage and utilization of industrial waste gypsum. BOU 46, NBRI, CSIR.

Lord, D.A. and N.D. Geldenhuys. 1986. Richards Bay effluent pipeline. South African National Scientific Programmes. Report No. 129. CSIR.

R & D, MANUFACTURING AND APPLICATION ASPECTS
OF
PHOSPHOGYPSUM

by

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This paper was presented by Mr S B Parikh in the "Second International Symposium on Phospho-gypsum" sponsored by the Florida Institute of Phosphate Research and organized by University of Miami held from December 10-12, 1986 at James L. Knight International Conference Centre, Miami, U.S.A.

ABSTRACT

The paper discusses comprehensively the R&D, Manufacturing and Application aspects of Phospho-gypsum technology. It describes the GSFC's plant experiences and findings concerning effects of various rocks, operating conditions in various sections such as digestion, filtration, concentration, gypsum purification etc. The effect of process upgradation In PA plant is also dealt with. The similar effects especially with respect to ammonium sulphate manufacture from phospho-gypsum in AS plant and its integration with PA plant have been described. The process simulation R&D work on conversion of phospho-gypsum to ammonium sulphate with regard to reaction kinetics, crystallography, and operational variables like temperature, excess ammonia, recycling of magma etc. have been illustrated. The R&D aspects of byproducts phosphogypsum with the objectives of higher productivity of PA/SA plants as well as diversification programme through the new developments of industrial applications of phosphogypsum especially for wall boards in building construction etc. have been covered.

INTRODUCTION

There is an increasing trend for utilizing byproduct phosphogypsum instead of disposing of, in the present time because of the advent of new chemical industrial. and agricultural applications and availability of new technologies, opening up of new market, dwindling supply of natural gypsum, rendering techno-economics of its utilization favourable on one hand; and dangers of air, water and land, pollution, requirements of compliance of local legislation, scarcity and high cost of land etc., causing gypsum disposal more and more difficult on the other. However, phosphogypsum is known to have complex behaviour because of its composition and characteristics attributable to its own intrinsic properties and associated impuritues derived from characteristics of parent raw material viz. rock phosphates, and processing conditions it is subjected to. This calls for indepth study of various R&D manufacturing and application aspects of phosphogypsum together, which are closely interrelated and how successfully they are employed determines the success or failure of the processer of phosphogypsum.

GSFC is manufacturing good quality phosphogypsum in its P.A Plant and converting it into ammonium sulphate fertilizer successfully since 1967 and its R&D aspects are studied in the Research Centre. Incidently, the author has been associated with all these three aspects of phospho-gypsum and hence chosen the comprehensive subject matter viz.

"R&D, MANUFACTURING AND APPLICATION ASPECTS OF PHOSPHOGYPSUM" for this international symposium on Phosphogypsum. The paper deals with actual theoretical and practical experience and findings of GSFC's P.A. Plant, A.S. Plant and R&B Centre on Phosphogypsum.

1. Manufacturing aspects of Phosphogypsum.
   - Brief description of GSFC's P.A Plant
   - Manufacturing factors effecting quality of byproduct phosphogypsum.
     a) Effect of types of rocks
     b) Effect of operating conditions of gypsum
     c) Effect of process upgradation of gypsum.

Application aspects of byproduct gypsum.

- Process description of GSFC's A.S Plant
- Effect of gypsum quality on A.S Production.
- Inter-relation between manufacturing an application aspects of phosphogypsum.

R&D aspects of phosphogypsum.

- Process simulation R&D work on reaction kinetics of conversion of phosphogypsum to ammonium sulfate.
  a) Reaction kinetics
  b) Crystallographic effect on time of conversion
  c) Effect of temperature
  d) Effect of agitation
  e) Effect of recycle magma
  f) Effect of excess ammonia.

Diversification to new application of Phosphogypsum especially in manufacture of plaster and wallboards.

The above text is substantiated by a number of sketchs, tables, diagrams and graphs.

R & D, MANUFACTURING AND APPLICATION ASPECTS
OF
PHOSPHOGYPSUM

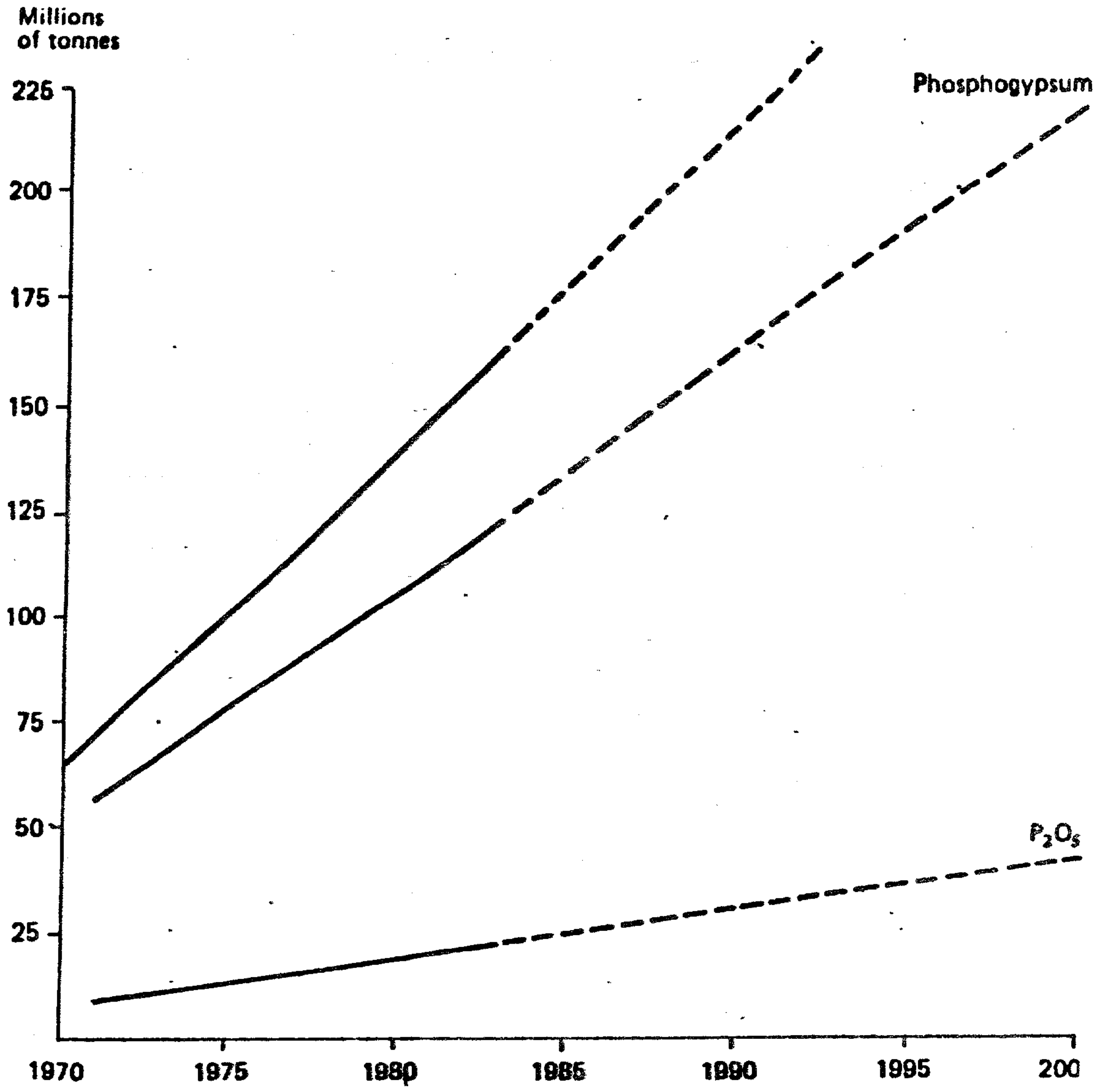
Gypsum ($CaSO_4$-$2H_2O$) as such is known to have complex behaviour because of its composition and characteristics attributable to its own intrinsic properties and associated impurities. This is universally experienced with natural mined gypsum and much more so with the phosphogypsum (a byproduct of phosphoric acid manufactured from rock phosphate and sulphuric acid) because of the added complexity contributed by the parent raw material rock, which in turn is known to have complex characteristics and also processing conditions it is subjected to. So much so the manufacture of phosphoric acid which is a basic material for phosphatic fertilizers, is controlled by gypsum that the technology of P.A is essentially called a technology of gypsum although it is a byproduct and ironically in most of the cases it is disregarded as waste product. As under manufacturing, under application too, gypsum is controlling whether it is put to chemical applications such as conversion to ammonium sulfate fertilizer or industrial applications such as conversion to plaster or wall board or cement/sulphuric acid manufacture.
It is therefore logical that there lies a close interrelationship between R&D, Manufacturing and Application aspects of Phosphogypsum and the consequences may be good or bad for a processor depending upon how well one has understood them and skillfully employed.

In GSFC, successfully, a good quality gypsum is manufactured in its Phosphoric Acid Plant; converted to Ammonium Sulphate Fertilizer in its A.S Plant; and its R&D aspectsare studied in its R&D Centre. Incidently the authors have been associated with all these three aspects and it is in this context that the comprehensive subject matter viz. **"R&D, Manufacturing and Application aspects of Phosphogypsum is chosen for this International Symposium on Phosphogypsum.**

The present scenario of phospho-gypsum poses great challenges and offers opportunities for manufacturers, users and researchers in the field. As per the estimated and projected worldwide production of phosphogypsum (Fig.1), the present production level of phosphogypsum from 120-150 Million MT is likely to increase to 150-200 Million MT by 1990's. All these gypsum can either be put to industrial use, either for the manufacture of ammonium sulfate fertilizer, plaster and wall board, cement sulphuric acid or in the cement production or to agricultural use in amendment or in reclamation of soil. Alternatively, it has to be disposed of - either to be discarded into sea or river, piled up into excavated mines or quarries or dumped into open land or settling pond. There has been increasing problems in gypsum disposal such as dangers of land, water and air pollution; requirement of compliance with local legislations, threat to aquatic life and normal water supply, dust nuisance to public, scarcity and high cost of land etc. On the other hand, advent of new technologies, opening up of new market, dwindling supply of natural gypsum, improving techno-economic of gypsum utilization

Figure 1.

Annual world production of P_2O_5 and phosphogypsum, 1970 – 2000



etc. are favourable factors for exploring its profitable application. In 1970, nearly all the byproduct gypsum was disposed of; in 1975, around 10% of the available gypsum was put to use, and this was increased to around 15% in 1980's. This shows a definite trend of growing interest in the alternative of using byproduct gypsum rather than disposing it of. This paper in this symposium, therefore, has a special relevance and importance, since it deals with the actual theoretical and practical experiences and findings of GSFC's P.A Plant, A.S Plant and R&D Centre on Phosphogypsum.

MANUFACTURING ASPECTS OF PHOSPHOGYPSUM.

BRIEF PROCESS DESCRIPTION OF PHOSPHORIC PLANT AT GSFC.

GSFC's dihydrate wet process P.A Plant has the design capacity of 165 MTPD P_2O_5 in form of 45% P.A. When commissioned in June 1967, it was India's largest single stream plant. The plant is designed by Chemico and is supplied on turnkey basis by M/s Hitachi Zozen. After carrying out two successful debottleneckin and capacity up programmes, today the achievable capacity is around 205-210 MTPD P_2O_5.

As shown in Fig. 2, the plant is divided in five sections:

1. Rock handling and grinding
2. Digestion
3. Filtration
4. Concentration, and
5. Gypsum purification.

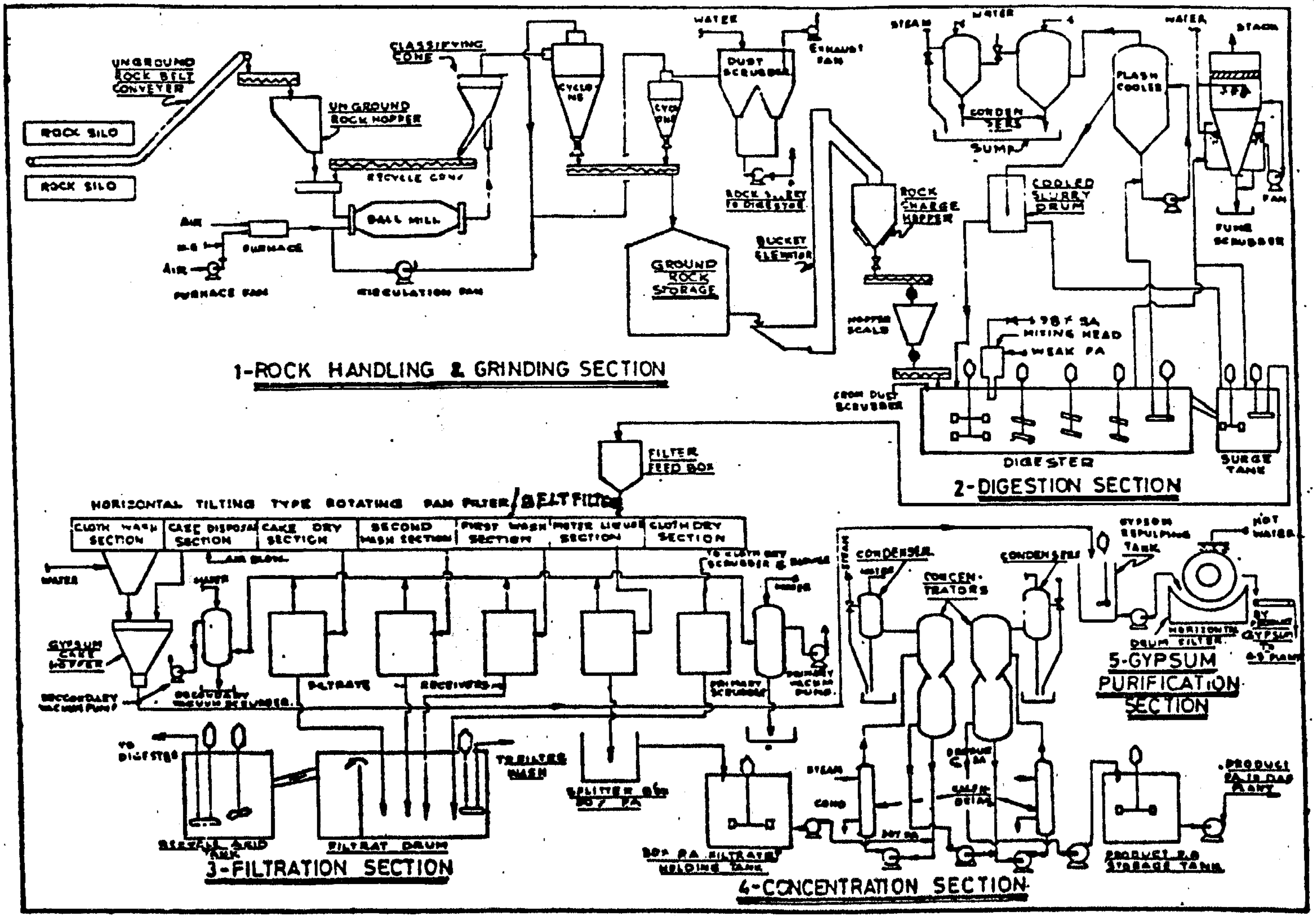


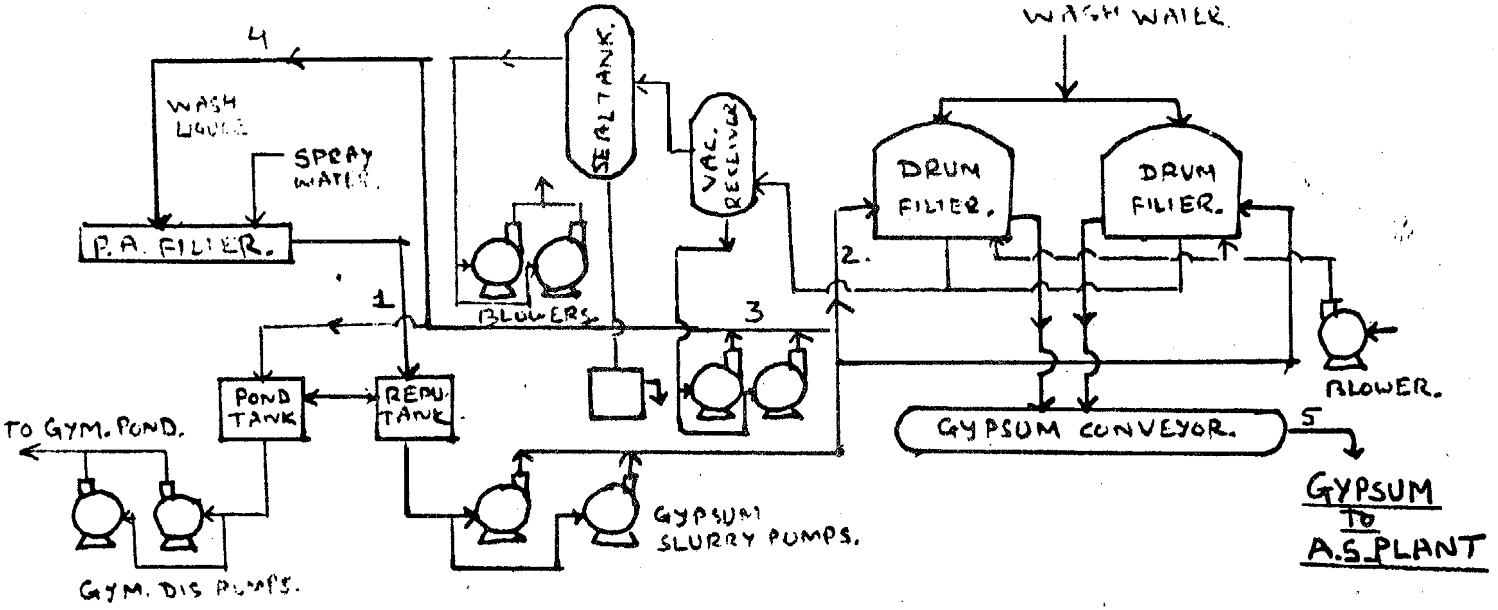
Figure 2—Process flow diagram of GSFC's phosphoric acid plant.

Unground rock is grounded in Ball Mill to 60% through 200 mesh and 100% through 40 mesh size through closed circuit dry grinding. In digester which is two stage, single tank reactor, ground rock is charged through Hardy scale. Also 98% sulphuric acid from GSFC's own S.A Plants and 17% recycled weak P.A from filtration section after mixing in a Mixing Head are fed to the Digester.

Heat of reaction is removed in a flash cooler. In the original system, horizontal, tilting pan type EIMCO Filter is provided where filtration of 30% PA Gypsum slurry is carried out through successive stages of filtration, washing, cake drying, cake discharging and cloth drying. 30% filtrate P.A. is taken to filtrate holding tank and 17% weak PA is recycled to Digester. Recently in 1984, a Delkor type Belt Filter from M/s Delfilt U.K is installed as part of capacity up programme. GSFC is first to install and use Belt Filter for PA manufacture in India. 30% P.A is subsequently concentrated to 40% PA in two stage single effect struther's type concentrators provided with Karbate tube Calendria. Product PA is stored in CSRL storage tanks and pumped to Di-ammonium Phosphate Fertilizer Plant.

Gypsum purification section.

Because of its relevance, this section, specifically, is described in detail (Ref. Fig.3)



CONSTITUENTS T/H	1	2	3	4	5
P_2O_5	0·104	0·089	0·057	0·042	0·032
H_2SO_4	0·008	0·008			0·008
H_2SiF_6	0·008	0·008			0·008
H_2O	48·475	41·509	42·878	30·718	9·041
$CaSO_4 \cdot 2H_2O$	30·514	26·153			26·153
FLUOSILICATES.	0·330	0·283			0·283
INSOLUBLES.	1·197	1·026			1·016
TOTAL T/H	80·640	69·076	42·935	30·760	36·551

FIGURE-3. GYPSUM PURIFICATION SECTION (P.A. PLANT).

Gypsum from filtration section is in the form of cake containing about 20-25% moisture and is subjected to purification in this section to reduce its soluble P_2O_5 impurities to improve gypsum quality for better operation of subsequent Ammonium Sulphate manufacture in A.S Plant and to improve economics of PA manufacture by recovering costly P_2O_5.

The gypsumcake is sluiced by high pressure water spray and is received as 40% gypsum slurry in an agitated repulping tank. It is then filtered on the Drum Filters using polypropylene multifilament filter media. The gypsum cake is further effectively washed by hot water spray through a series of spray nozzles. It is subsequently dried, blown and scrapped off the filter onto belt conveyer which either conveys it to A.S Plant or dumps in the gypsum storage yard.

The soluble P2O5 recovered from gypsum cake goes in the filtrate which is collected in filtrate receivers and recycled to filter section to be used as wash liquor. Gypsum chemical analysis as per design before and after purification is given in Table-I. A typical screen analysis is given in Table-II

Manufacturing factors affecting quality of byproduct gypsum.

In a given P.A Plant, quality of byproduct gypsum is mainly affected by type of the rock-phosphate used; operating plant conditions; and plant design conditions. GSFC's experience is dealt below:

TABLE - I

DESIGN GYPSUM ANALYSIS BEFORE AND AFTER PURIFICATION
(Per cent, dry basis)

Components	Gypsum analysis	
	Before purification (from pan filter)	After purification (from drum filter)
Soluble P_2O_5	0.324	0.116
Total P_2O_5	1.114	0.906
$CaSO_4 2H_2O$	94.868	95.076
H_2SO_4	0.025	0.025
H_2SiF_6	0.025	0.025
Silica	2.807	2.807
Na-K Fluosilicates	1.028	1.028
Fe_2O_3, Al_2O_3	0.133	0.133

TABLE - II

SIZE ANALYSIS OF GYPSUM

Mesh size (Tyler)	Per cent classification
+ 40	2.5
+ 80	3.5
+ 100	4.0
+ 150	24.0
+ 200	15.0
- 200	51.0

Effect of type of rocks on gypsum.

GSFC's P.A Plant is designed on the basis of 72 BPL Florida rock. As per design the P_2O_5 recovery is about 95% with considered P_2O_5 losses as:

(a) 3% P_2O_5 - as $CaHPO_4$, substitution loss in gypsum crystal lattice.

(b) 0.5% P_2O_5 - as $Ca(PO_4)_2$ in the form of unreacted rock joining in gypsum.

(c) 1.5 P_2O_5 - as soluble P_2O_5 in the form of liquid in gypsum cake.

It may be noted that GSFC is unique in the world to have processed record number of rocks and rockblends on large and varied scale in its P.A Plant. The plant was designed on Florida; it was commissioned on Morocco; it has run maximum on Udaipur blends of 1:1 and it has registered highest production on Senegal. Since it went on stream in June 1967, till today, it has processed for shorter or larger period, as many rocks as Florida, Udaipur, Senegal, Morocco, Algerian, high grade Jordan, low grade Jordan etc. and as may rock blends as Udaipur : Florida 1:1, Udaipur : Senegal 1:1, Udaipur : Morocco 1:1, Florida : Senegal 1:1 etc. This was mainly due to availability and also plant suitability considerations. Of course, for quite some time, Senegal rock is being consistently used. The composition of various rocks and rock blends is given in Table-III.

TABLE - III

COMPOSITION OF ROCKS AND ROCK BLENDS PROCESSED IN GSFC.

Sr No.	Rocks & Rock Blends.	Average composition (dry basis)										
		P_2O_5	CaO	SiO_2	F	Al_2O_3	Fe_2O_3	Na_2O	SO_3	LOI	CO_2	Chloride (ppm)
1.	Senegal	36.80	51.51	2.97	3.93	1.21	0.67	0.30	0.29	2.45	1.61	28
1.	Udaipur	36.21	50.26	7.35	3.39	1.30	0.73	0.10	Traces	1.18	1.04	25
2.	Florida	33.16	48.14	4.91	3.89	1.14	0.70	0.45	0.80	5.08	2.60	44
3.	Morocco	32.63	50.52	2.34	4.11	0.54	0.15	0.76	1.81	6.86	4.01	255
4.	Algeria *	33.78	54.13	1.4	3.67	0.41	0.32	-	-	-	-	-
5.	High grade Jordan	34.35	52.65	1.29	4.07	0.20	0.20	0.41	1.04	6.39	3.99	177
6.	Low grade Jordan.	32.75	51.26	4.45	4.00	0.35	0.30	0.40	0.95	8.41	6.20	2800
1.	U:F 1:1	34.44	49.40	5.07	3.62	1.22	1.12	0.35	0.64	2.94	2.08	40
2.	U:S 1:1	35.79	50.90	5.53	3.56	0.66	0.80	0.14	Traces	2.41	1.62	28
3.	U:M 1:1	34.49	50.52	5.15	3.60	0.87	0.69	0.36	0.82	3.93	2.91	262
4.	S:F 1:1	34.37	49.08	3.68	3.50	1.23	1.00	0.23	0.36	-	2.30	50

* Used in the initial stages for short period.

CaO/P_2O_5 ratio in rock determines quantity of gypsum per MT of P_2O_5. How this ratio and accordingly relative quantity of gypsum varies with changing of rocks is shown in Fig-4.

Silica, Ra20, etc., impurities if higher in rock, give rise to higher acid insolubles in gypsum. Organic impurities in rock affects colour of gypsum. Average composition of byproduct gypsum with various rocks and blends is given in Table-IV. Due to higher Silica content gypsum from Udaipur rock containing rock-blends have higher acid insolubles impurities in gypsum.

Effect of operating conditions on gypsum.

Digester operating conditions in PA Plant has been experienced as the key factor determining gypsum crystallography which controls the reaction and filtration and thereby production, efficiency and stream days and hence techno-economics of PA plant. Temperature and free sulphuric acid are very important operating conditions determine crystallography. Temperature of course is fixed depending upon the process route, which is around 75 to 80°C for dihydrate process. For the best results the gypsum crystals should be ideally filterable and washable of P_2O_5. It has been observed that crystal shape and size have bearing on filterability and washability and Rhombic shape length to breadth ratio of nearly 3:1 give high filterability and washability. After a number of trials,. free S.A level between 2 to 3% in digester has been optimized as the one giving best results. Other conditions such as slurry density,

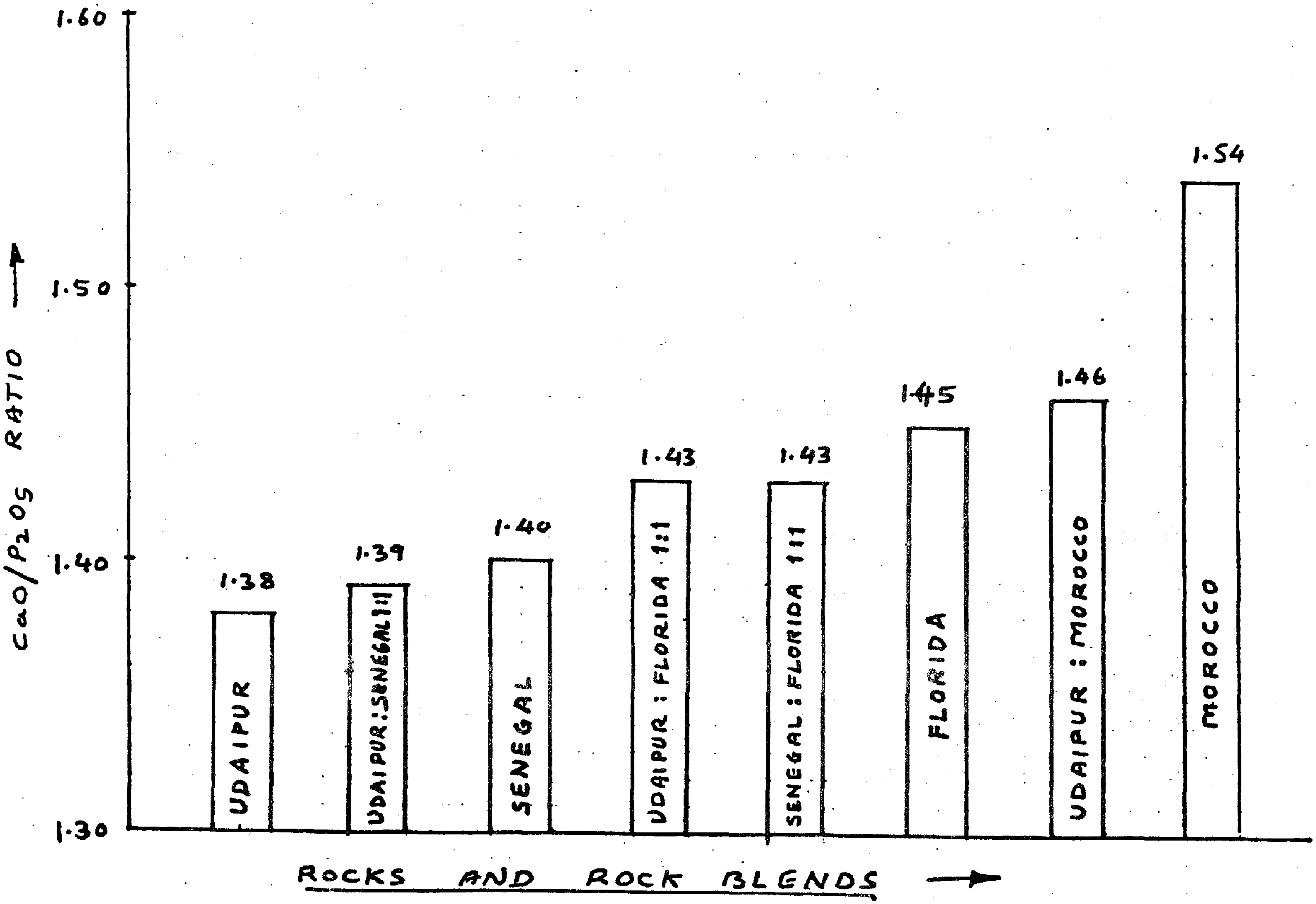


FIG. 4 CaO/P_2O_5 VARIATION IN ROCKS AND ROCK BLENDS

TABLE - IV

AVERAGE COMPOSITION OF BYPRODUCT GYPSUM (Per cent)

Rock	Moisture	Dry basis			
		Acid insoluble	$T-P_2O_5$	Acidity	Gypsum $CaSO2H_2O$
Florida	17.35	2.27	0.749	0.314	96.30
Udaipur	19.96	3.09	1.430	0.449	94.80
Morocco	23.09	0.90	1.010	0.702	97.30
Senegal	20.45	1.41	0.792	0.276	92.05
F:U::1:1	21.04	4.37	0.798	0.228	94.00
M:U::1:1	18.85	2.80	0.863	0.222	96.30
S:U::1:1	18.64	3.61	0.685	0.269	94.96

liquid/solid ratio may affect physical characteristics with regard to moisture etc. of the gypsum which has affected transport and handling characteristics.

GSFC had to change number of rocks and rock blends all varying in characteristics. This required change in operating conditions with regard to slurry density, slurry filtrate density, free sulphuric acid, recycle acid density, etc. GSFC had to work extensively to establish and optimize operating conditions in each case (Ref. Table-V). It may be noted that in spite of all these, PA plant has maintained high performance records in terms of PA production and supply of good quality gypsum to A.S Plant (Also Ref. Table VIII and Fig-7).

Effect of process upgradation on gypsum

In the original plant design, for PA Gypsum slurry filtration, EIMCO type horizontal, tilting pan filter Was provided. It had process, operation and maintenance problems which limited P.A Plant production, P_2O_5 efficiency, stream days and gypsum quality. In 1984, GSFC installed a Delkar make horizontal Belt Filter from M/s Delfilt, U.K. This is the first installation of Belt Filter in P.A Plant in India. Compared to existing Pan Filter, Belt filter had no air leakage and better maintaining of vacuum, better air flow through filter, higher filtration rate, better cloth washing efficiency due to continuous separation of cloth from belt during each cycles and lower maintenance due to better design and engineering. As seen from Table-VI, after installation of Belt filter, there was a significant improvement

TABLE - V

AVERAGE DIGESTER CONDITION WITH VARIOUS ROCKS

Rock used	Slurry density	Slurry filtrate density	Free sulphuric acid.	Recycle acid density	Flash cooler vacuum mmHg	Digest temp.°C
F:U::1:1	1.57	1.32	2.20	1.20	600	76.0
M:U::1:1	1.56	1.31	2.19	1.20	590	76.0
S:U::1:1	1.53	1.29	2.28	1.15	610	74.0
Florida	1.57	1.30	2.62	1.17	650	73.0
Udaipur	1.54	1.29	2.04	1.18	650	75.5
Senegal	1.563	1.32	2.22	1.18	660	77.0
Morocco	1.56	1.31	2.30	1.22	615	75.0

TABLE - VI

IMPROVED P.A. PLANT & A.S. PLANT PERFORMANCE AFTER INSTALLATION OF BELT FILTER IN P.A. PLANT

Sr No.	Item	Pan Filter	Belt Filter
1.	P.A. Plant production level MTPD - P_2O_5	170	205
2.	<u>Gypsum quality</u>		
	i) T-P_2O_5 (%)	0.6 to 0.7	0.5 - 0.6
	ii) Soluble P_2O_5	0.2 - 0.3	0.15 - 0.20
	iii) Screen analysis (Mesh size B.S)		
	+ 100	10.0	2.5
	+ 150	24.0	10.5
	+ 200	15.0	34.0
	- 200	51.0	53.0
3.	A.S Plant production level, MTPD A.S	470	530

in P.A production level which increased from average 170 MTPD P_2O_5 to around 205 MTPD P_2O_5 level and side by side improved gypsum quantity as well as quality. The gypsum analysis running Belt filter indicated P_2O_5 around 0.1-0.2% compared to around 0.2 - 0.5% in case of Pan Filter. Since the rock used being of same quality, the size analysis remained nearly same. The increased gypsum quantity and improved quality increase production performance of ammonium sulphate plant also remarkably from average production level of around 470 MTPD to around 530 MTPD.

APPLICATION ASPECTS OF BYPRODUCT PHOSPHOGYPSUM

Process description of GSFC's Ammonium sulphate plant.

Byproduct gypsum from P.A Plant is converted to the useful Ammonium Sulphate Fertilizer in the Ammonium Sulphate Plant. This plant based on ICI-Chemico's process is designed by Chemico and supplied on turnkey basis by Hitachi Zozen, Japan. It has the design capacity of 470 MTPD A.S and in 1967 when it went on stream, it was the then largest successful plant of its kind converting waste gypsum into useful fertilizer in the world. Number of personnel in the field of gypsum conversion to A.S have taken training in start up and plant operation, in this plant including a team of engineers from Bulgaria.

Chemistry

First Ammonium Carbonate solution is prepared by reacting aqueous solution of ammonia with CO_2.

$$2NH_3 + CO_2 + H_2O - (NH_4)_2 \ CO_3$$

$$H \quad = + 22.08 \text{ K. Cal/Mole.}$$

This is then reacted with gypsum to give ammonium sulphate liquor and calcium carbonate (chalk)

$$(NH_4)_2CO_3 + CaSO_4 \ 2H_2O \text{ -- } (NH_4)_2 \ SO_4 + CaCO_3 + 2H_2O$$

$$H \quad - 2.7 \text{ K. Cal/mole.}$$

Process.

The A.S Plant is divided in following sections (Ref. Fig.5) (a) Carbonation (b) Reaction (c) Filtration (d) Decomposition (e) Evaporation and (f) Centrifuging and Drying.

In view of around 20% moisture in purified gypsum cake from P.A Plant, high concentrated i.e. 55% by wt. solution of $(NH_4)_2 CO_3$ is first prepared to reduce evaporation load. For this, ammonia and CO_2 are reacted in Carbonation tower. Feed ratio of $CO_2 : NH_3$ is maintained around 1.35. Pressure is around 1.4 kg/cm^2 in the tower and temperature is about 40-65°C.

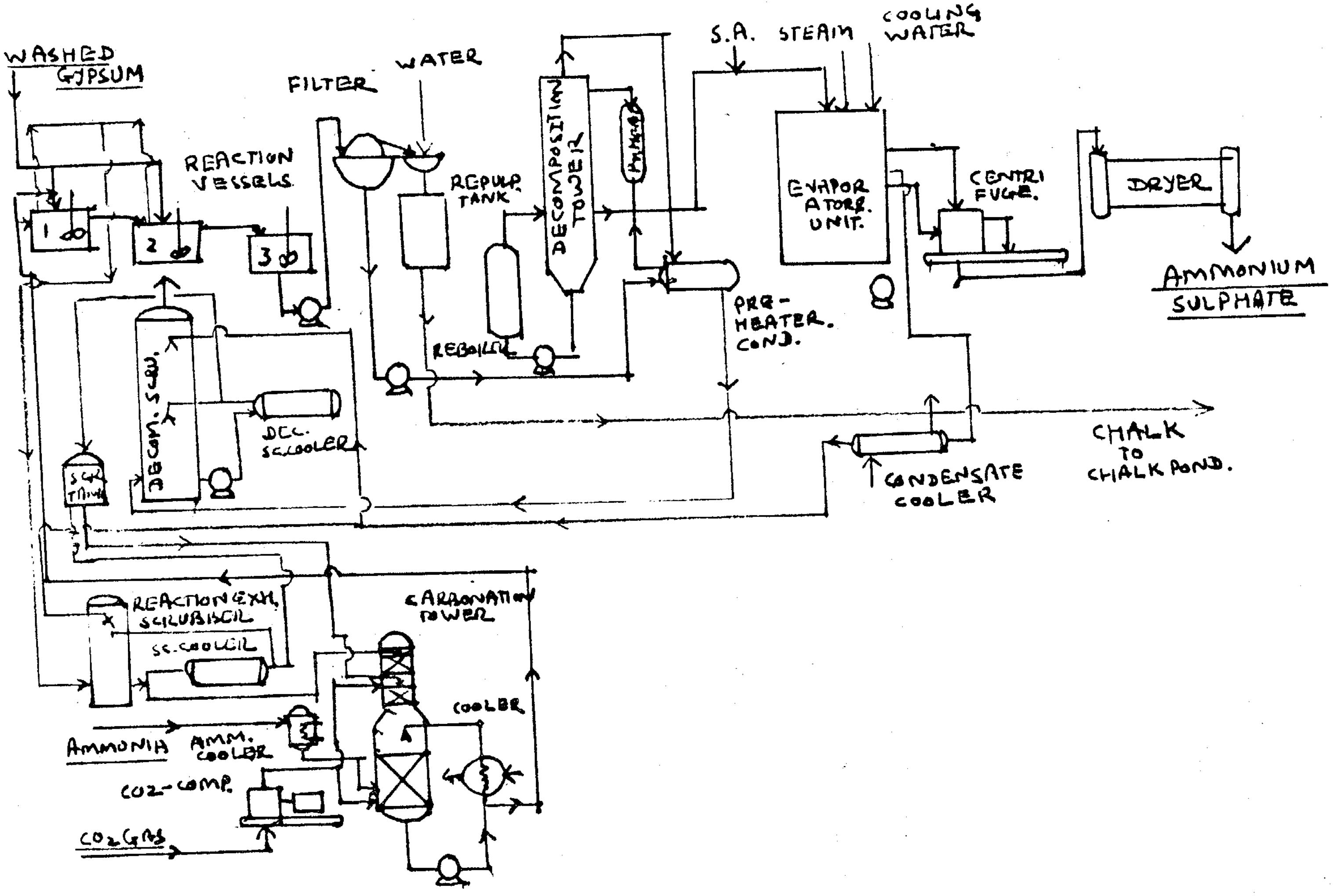


FIGURE-5. AMMONIUM SULPHATE PLANT FLOW DIAGRAM.

Gypsum is weighed, repulped in Vortex Mixer with recycled megma and fed to the first reaction vessel. There are three agitated vessels operating in series and indirectly heated by steam. Gypsum slurry and carbonate liquor are reacted to form magma. In order to optimise the endothermic reaction, the temperature in first vessel is kept about 60°C and 70-73°C in subsequent vessels. Part of magma from third vessel is recycled to first and rest is sent to filtration section.

Filtration is carried on primary and secondary rotary type filters. Multifilament polypropylene cloth is used as filter media, The loss of A.S in chalk in primary filter is minimised by giving hot condensate wash to chalk. Strong A.S. liquor from filter is sent to chalk settler to remove any remaining solids. The chalk from filter is repulped and sent to chalk pond. The strong liquor contains small amounts of free ammonia and CO_2 which are removed in the Decomposition Section by heating with steam. Cooled gases are absorbed in the condensate. The decomposed liquor is sent for evaporation. Evaporation is carried out in tripple effect, forward feed Oslo type evaporator crystallizers. The slurry is then fed to the centrifuge where A.S. crystals are separated from mother liquor. Crystals are dried in rotary type drier and sent for bagging.

Raw materials and utilities requirement.

Raw material and utilities requirement per MT of A.S are:

			M.T
a)	Gypsum	..	1.45
b)	NH_3	..	0.305
c)	CO_2	..	0.405
d)	Steam	..	1.25
e)	Cooling water	..	70
f)	Process water	..	3.2
g)	Natural gas	..	70,000 K.Cal.

Product specifications.

Ammonium sulfate in crystalline form has following specifications:

		% by w.t.
Nitrogen content, min	..	20.6
Free acidity as H_2SO_4, max.	..	0.025
Moisture, max.	..	0.25
Screen analysis (Bs)		
- Mesh, max.	..	5
+ Mesh, max.	..	5

Effect of gypsum quality on A.S. production.

Various impurities in gypsum affects reaction and filtration of A.S. as follows:

(i) P_2O_5

Ammonium carbonate reacts preferentially with phosphoric acid or phosphates present in the gypsum. Free P.A reacts with Ammonium Carbonate to give Ammonium Phosphate and this in turn, reacts with gypsum to give Calcium Phosphate. This simultaneously reacts with more gypsum to form insoluble tricalcium phosphate, which due to its gelatinous state reduces filtrability of $CaCO_3$ - A.S. slurry. If any soluble phosphate remain, they disturb the reaction of gypsum with Ammonium Carbonate and give a resulting Calcium Carbonate which is extremely fine, partly colloidal and Thixortropic. It may render filtration extremely difficult. Fig. 6 shows how P_2O_5 content in gypsum affects filtration rates. Free P.A also increases corrosion rate.

ii) Fluorine

Fluosilicic acid and P.A cause foaming which may result in overflow losses from reactors. They also increase corrosion rate.

iii) Silica

Fine silica interfers with filtration. Sodium and Potasium fluosilicates affect filtration by limiting crystal growth and clogging filter cloth. It may increase erosion.

iv) Organic impurities.

It causes foaming and sometimes discolouration of final product.

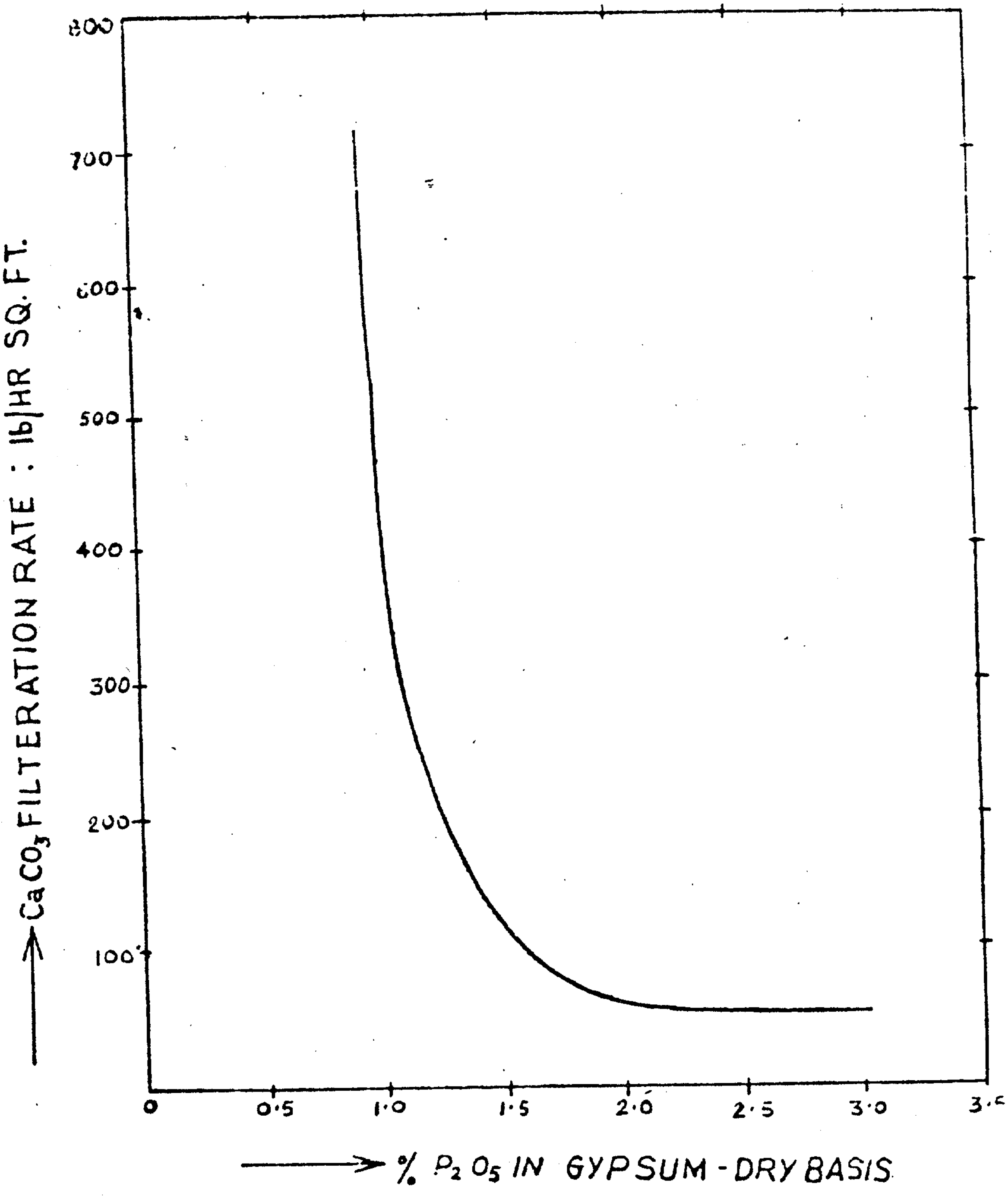


Figure 6—Effect of P_2O_5 in gypsum fed to convertor on calcium carbonate filtration.

v) Size of gypsum particles.

Chalk of good filtering characteristics posses approximately the same particle size distribution as the gypsum from which it is produced. A course gypsum produces a chalk of fairly good filterability but gives a poor conversion of gypsum to A.S. The finer the gypsum, the better the conversion rate, however, the poorer filterability. In particular, the filtering rate becomes very slow when particle size falls below 20 microns. Gypsum size between 60 and 100 mesh gives the optimum best reaction and filtration conditions.

These effects have been one or the other time practically experienced. 'Due to high moisture content, problems of conveying gypsum on belts and through hoppers are substantial and throughput of gypsum had to be reduced. As in case with Udaipur or Morocco rocks, the phosphogypsum, due to high P_2O_5 content affects reaction and filtration of ammonium sulphate. The reaction magma deteriorates and time of revival may increase from normal 3 to 4 hours to about 12 to 22 hours. Size analysis of a typical good and poor magma which does not settle easily is shown in Table-VII. This in turn, has reduced filtration rate from normal 40 M^3 A.S liquor/hour to about 2 to 3 M^3/hour. Fine chalk carried over has increased rate of choking of reboilers and calendria in evaporation section. The acidic impurities have caused foaming and reactors overflow. Silica has increased erosion of pump impellers.

TABLE - VII

SIZE ANALYSIS OF REACTION MAGMA (Per cent)

Size analysis	Reaction magma	
	Good condition	Bad condition
+ 100	10.0	1.4
+ 150	21.2	3.6
+ 200	20.8	8.0
- 200	48.0	87.0

The overall effect is such that in case of inferior gypsum of Udaipur or Morocco, A.S. production is hampered whereas with good quality gypsum as in case of Senegal or Florida: Udaipur 1:1 blend, A.S. Plant has registered record production.

Inter-relationship between manufacturing and application of phosphogypsum - successful co-ordinated running of P.A and A.S Plants in GSFC.

GSFC's P.A and A.S. Plants are working in close co-ordination as far as Phosphogypsum is concerned.

Rocks used in P.A plant are of various types widely varying in composition. Even there was a wide variation in composition of a single type of rock. Moreover, GSFC used different rocks in blends. The problems were compounded due to non-consistent blend ratio and possible segregation of rocks in blend. It may be noted that in spite of such vagaries, GSFC has been able to produce good quality phosphogypsum consistently. This is seen from the statistical analysis of gypsum quality given in Table-VIII. This has contributed a great deal in achieving high production performance in P.A and A.S Plants. In recent years, with standardization to one Senegal rock, PA debottlenecking programme and installation of Belt filter (incidently with all of which the Authors are associated), there has been further improvement in P.A production and gypsum quality and quantity and so as in A.S production. A graph of annual production of P.A and A.S

TABLE - VIII

STATITICAL STUDY OF BYPRODUCT GYPSUM QUALITY

Month	Jan.	Feb.	March	May	June	July	Overall
No. of samples	29	29	39	28	27	31	175
$T\text{-}P_2O_5$ avg.	0.677	0.648	0.575	0.644	0.660	0.642	0.640
Standard deviation	0.183	0.138	0.175	0.228	0.197	0.117	0.175
Acidity avg.	0.246	0.229	0.129	0.261	0.290	0.197	0.232
Standard deviation	0.162	0.150	0.077	0.166	0.138	0.122	0.142

indicates that there is a substantial increase in production which has reached in 1985/86 record breaking level of around 105% and 110% of design capacity in P.A and A.S Plants respectively (Ref. Fig.7).

R&D ASPECTS OF BYPRODUCT PHOSPHOGYPSUM

R&D aspects of byproduct phosphogypsum are studied in GSFC's inhouse R&D Centre. Fertilizers is the key R&D activity because it being the key manufacturing and marketing activity of GSFC. R&D work related to Phosphogypsum has two main objectives:

i. to contribute to productivity of ongoing P.A/A.S plants through process simulation studies etc. and

ii. to contribute to diversification programme through development of new industrial applications especially plaster and wallboard.

In this regard, two R&D projects were undertaken which are described below:

Process simulation R&D work on reaction kinetics of conversion of phosphogypsum to ammonium sulphate.

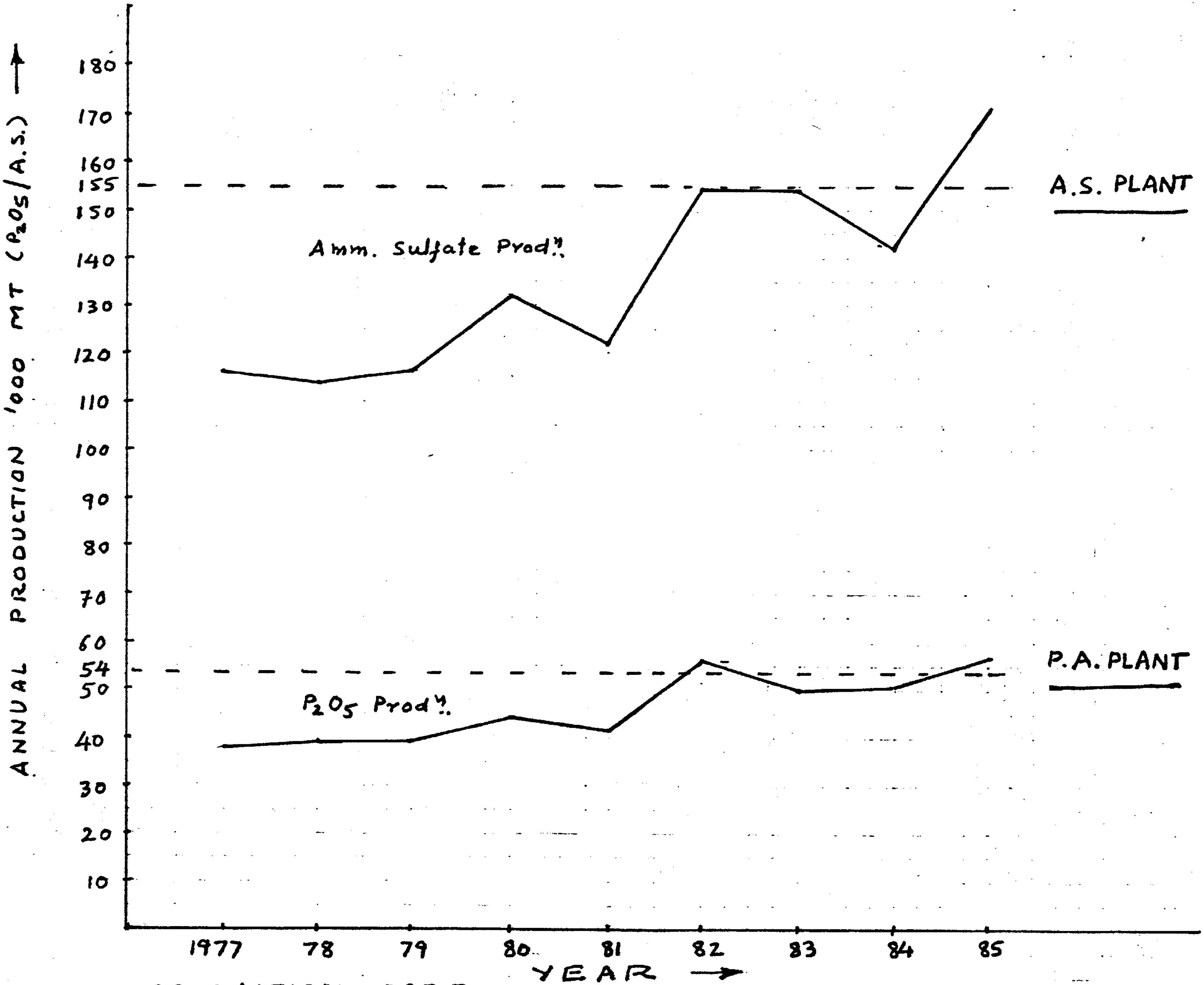


FIG. 7 PRODUCTION PERFOMANCE OF PHOSPHORIC ACID AND AMMONIUM SULPHATE PLANT

This process simulation R&D work was taken up with a specific objective to find out possible increase, if any, in gypsum conversion efficiency with increased residence time. This was required by A.S Plant for optimisation in ongoing plant; by Design Dept. for establishing basic design parameters for new expansion plant and management for techno-economic evaluation of investment proposals like providing new Reactor systems etc.

A.S Plant reaction sections conditions were simulated in R&D Centre. This consisted set up of reaction between phosphogypsum ammonium carbonate and magma at different residence time under varying condition of temperature, excess ammonia concentration and magma recycling. Feasibility studies, reaction kinetics, crystallography studies were made covering number of experiments and analysis. Only relevant aspects of this R&D work are described in brief.

Reaction kinetics.

In one typical case, two sets of experiments were performed at temperature 60°C and 67°C and conversion of gypsum to A.S was studied continuously for residence time upto above 3 hours at the suitable interval of 5 minutes initially and subsequently at the interval of 30 minutes. The individual reactions were arrested at the predetermined residence time interval and soon after followed by filtering and analysis of filtrate and cake.

The results of the kinetic study are given in Table-IX and graphically plotted in Fig.8.

The experimental results indicate that the reaction between gypsum and ammonium sulphate under plant simulation condition is initially fast and within a time of five minutes 93-95% of the gypsum is converted. Subsequently there is a slow increase in conversion. At existing residence time of 2.7 hours, the conversion was around 95-96% and there was an increase in conversion to 97-98% at proposed increased residence time of 3.2 hours. Thus there was 1-2% increase in conversion as residence time increased from 2.7 to 3.2 hours.

Crystallography.

Crystallographys studies indicated that unlike gypsum crystals which posses distinct shape and length/breadth ratios, the chalk crystals were fine and were agglomerated. There was an indication of increase in degree of agglomeration in the initial state of reaction is at 5/10 minutes and at higher residence time at around 2/3 hours.

Effect of temperature on conversion.

Reaction kinetics studies at temperature of 60°C and 67°C as described above indicated that there is practically no appreciable effect of temperature on conversion in this temperature range. The variation pattern of conversion at differ&t residence time was practically same.

TABLE - IX

REACTION KINETICS - EFFECT OF CHANGE OF RESIDENCE TIME ON GYPSUM CONVERSION

	Time Minutes	5	10	15	20	50	60	80	105	110	162	192	222
SET-1	% Gypsum conversion at reaction temperature 60°C.	93.53	95.69	97.87	96.12	95.23	-	95.55	-	96.67	95.29	97.6	97.3
SET-2	% Gypsum conversion at reaction temperature 67°C	95.48	94.60	97.46	97.68	96.04	-	94.55	-	96.75	94.90	96.39	97.31

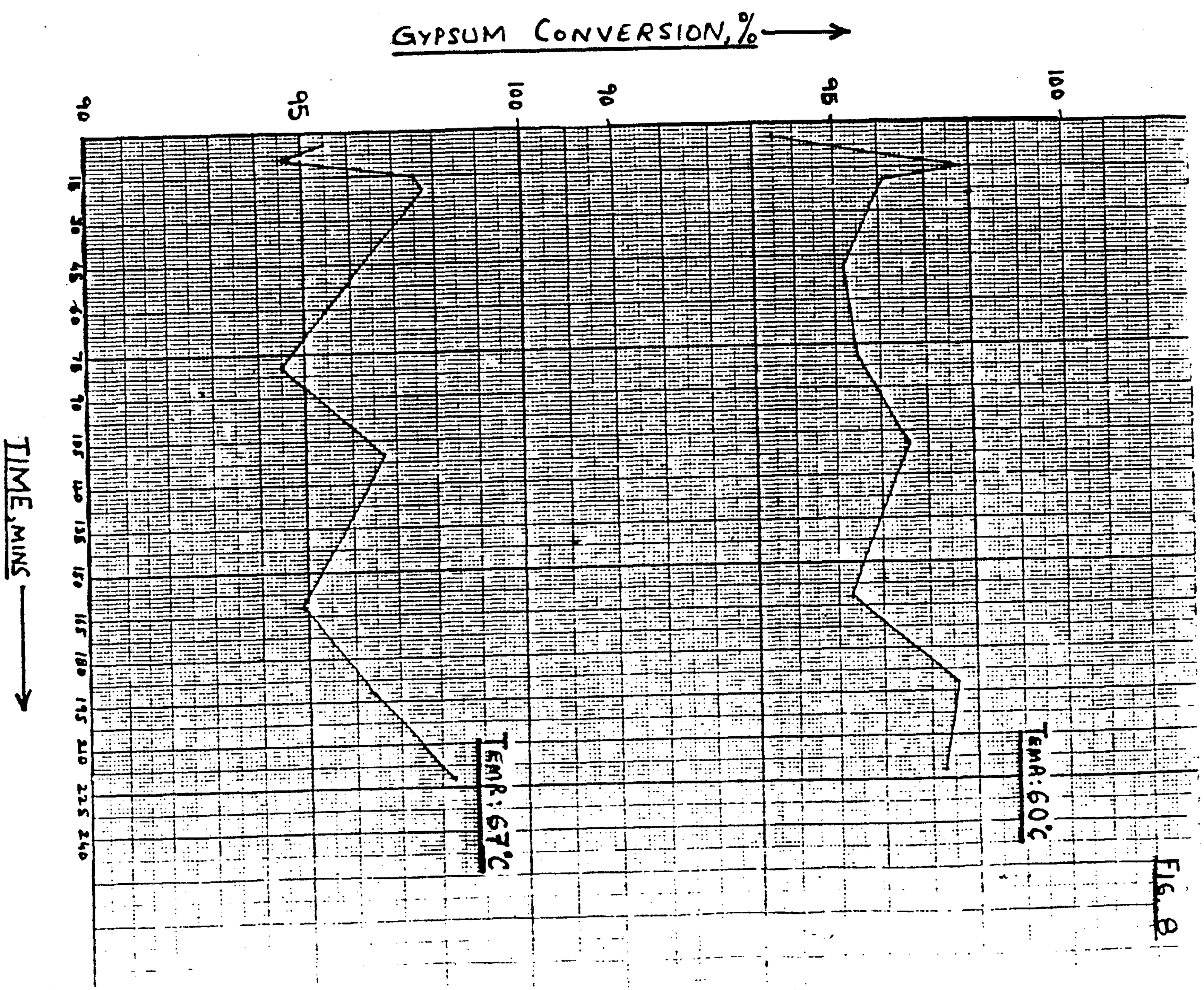

GYPSUM CONVERSION, %
90
95
100
90
95
100
TIME, MINS
15
30
45
60
75
90
105
120
135
150
165
180
195
210
225
240
TEMP: 67°C
TEMP: 60°C

FIG. 8

Effect of agitation.

Effect of agitation is important in the reaction mixing and qualitatively it was observed that gypsum conversion could drop substantially if the degree of agitation is low, probably due to coating of gypsum.

Effect of recycle magma.

In one set of experiment to study the influence of recycle magma; the research was carried out without using recycle magma. As was seen from the results of both the experiments, there was appreciable drop in gypsum conversion to 91-92%. This indicates that recycle of magma facilitates gypsum conversion. However, quality of magma will have bearing on gypsum reaction.

Effect of excess ammonia.

Excess ammonia is important variable in gypsum conversion. Percentage excess ammonia varied from 0 to 15%. The optimum % excess ammonia is around 7%. This was found to match with and confirm the recommended design condition.

It may be noted that above findings and due to recommendations by R&D Centre were useful to A.S Plant in optimisation; to design division in basic design and as a whole to the management in techno-economic evaluation of investment proposal and in corporate decision. To that extent, this R&D programme turned out to be of direct applicability and contributive. Further study in detail with regard to simulation, optimisation etc. are in progress.

Diversification to new application of phosphogypsum.

In India, so far phosphogypsum is not put to any other commercial use except in manufacture of A.S. Fertilizer or as agricultural use in land reclamation. R&D Centre is currently exploring the possibilities of using the phospho-gypsum especially in the manufacture of plaster and wall board for building construction. Preliminary techno-economics have been examined. Lab/Pilot Plant scale investigative work is being planned so as to assess and ascertain suitability of phosphogypsum for plaster and wall board and to adopt maximum indigenisation so as to render practically economical and suitable to Indian conditions.

CONCLUSION/RECOMMENDATIONS

There has been an increasing trend for utilising byproduct Phosphogypsum instead of disposing of. The attributable factors are advent of new chemical, industrial and agricultural application, availability of new technologies, opening up of new market and dwindling supply of natural gypsum on one hand; and danger of air, water and land pollution, requirement of compliance of local legislation, scarcity and high cost of land causing gypsum disposal more and more difficult on the other. However, phosphogypsum is known to have complex behaviour because of its composition and characteristics attributable to its Own intrinsic properties, associated impurities derived from parent raw material viz. rock phosphate and processing conditions it is subjected to. Hence there is a close interrelationship between R&D, Manufacturing and Application aspects of phosphogypsum. The indepth study and practical application of them determine success or failure of phosphogypsum processer. It is recommended that for the benefit of public; industries and Government, an international centre for Phosphogypsum dealing in its R&D, Manufacturing and application aspects be established.

ACKNOWLEDGEMENT

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REFERENCES.

UNIDO Publications, 1985. Utilisation of the Phosphogypsum produced in the Fertilizer Industry.

Industrial and Engineering Chemistry - Process Development Vol. 10.

International Fertilizer Development Centre, 1978 Fertilizer Mannual.

Slack, A.V. 1968. Phosphoric Acid

British Sulphur Corporation Publications.

DESIGN & OPERATING CRITERIA for a GYPSUM STACK/COOLING POND from an OWNER/OPERATOR'S POINT of VIEW

John E. Cameron, Project Specialist (1)
John J. O'Connor, Project Engineering Manager (1)

INTRODUCTION

At IMC-New Wales Operations, our gypsum stack is our single largest land user, with an area of over 400 acres at its base, But even at an anticipated operating height of 200 ft, it is projected that it will accommodate our gypsum disposal needs for only a few more years.

We are presently in the design/permitting stages of a two-phase stack expansion, to provide for gypsum disposal for the next 20 years at IMC-NWO, and suggest that it is not too soon to be planning for even 20 more years beyond that. All of us in the industry are hopeful that economic and useful purposes will be developed for phosphogypsum before that time. But so much gypsum is already stored in piles, and so much more is being produced, especially in Florida, that it is difficult to imagine that gypsum stacks will be completely eliminated in the future. So adequate planning for future gypsum disposal needs may be a matter of survival.

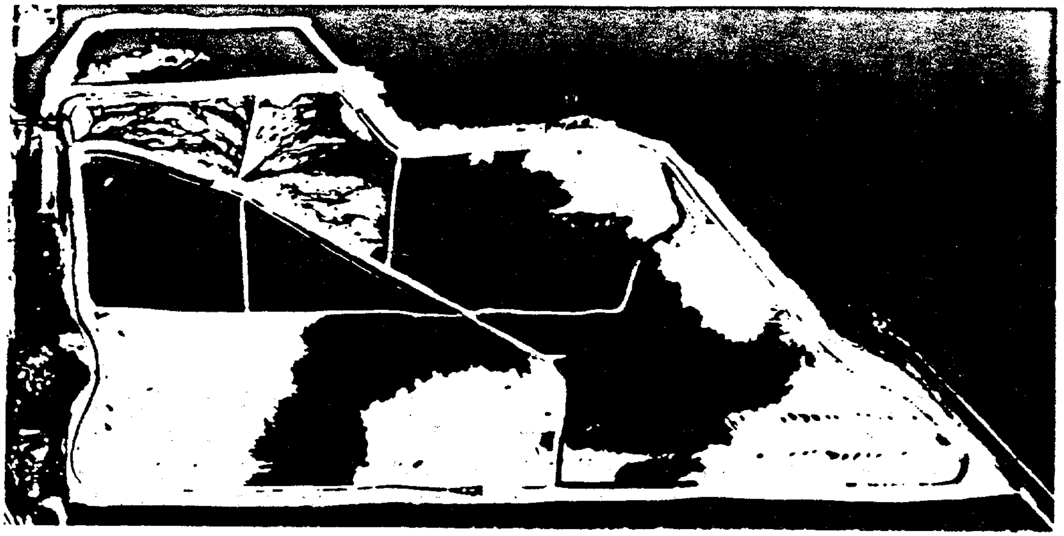
To properly discuss planning, we should also review the role of the gypsum stack in the total context of a phosphate chemical manufacturing operation. The following major topics are addressed in this paper:

OVERVIEW OF A TYPICAL(?) STACK
THE GYPSUM STACK'S ROLE IN COOLING
ITS ROLE IN PONDWATER BALANCE
FORECASTING WATER BALANCE
OPERATING A GYPSUM STACK
OPERATING CRITERIA FOR MAINTAINING A GYPSUM STACK
STORAGE REQUIREMENTS FOR GYPSUM
LAND PLANNING FOR GYPSUM STACKS

OVERVIEW OF A TYPICAL(?) GYPSUM STACK

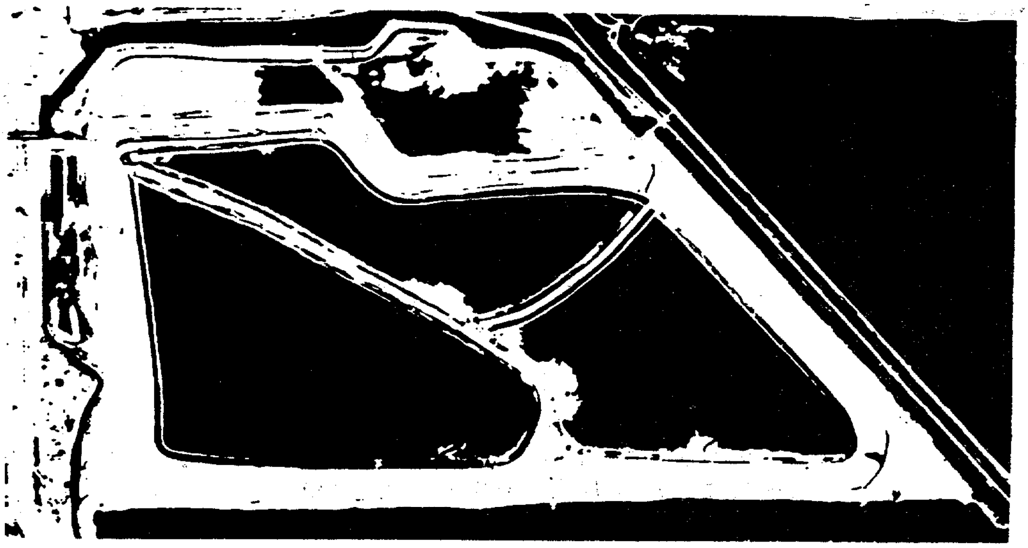
Most of the properties and statistics presented in this paper pertain to by-product phosphogypsum produced at IMC's New Wales Chemical plant, in Polk County, Florida. New Wales' gypsum is in the dihydrate form.

(1) International Minerals & Chemical Corporation, New Wales Operations, Mulberry, Florida



1979 Aerial Photo - IMC-NWO Gypsum Stack

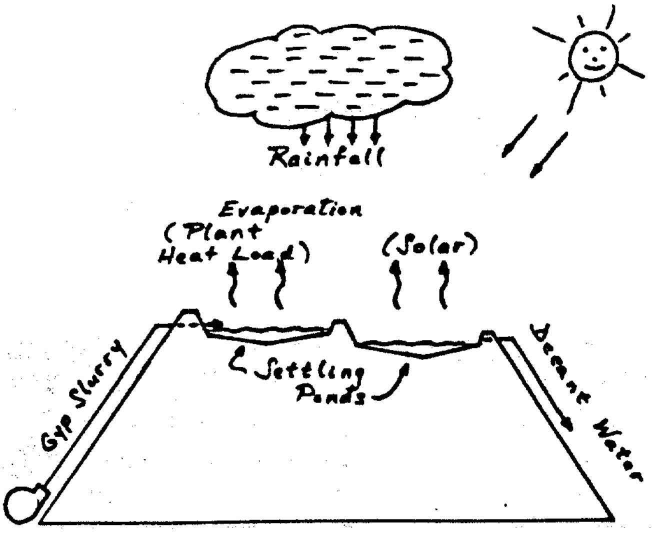
Seven years ago, our gypsum stack consisted of a hodge-podge of 8 active settling areas, with a total area of about 350 acres at its top. At less than 20 feet high, we could still convey the gypsum slurry from our filters by gravity to the top of the stack, without pumping. Many of the crossdams were not rim ditched, and water coverage was generally very poor. We had a very wet September in 1979, and our cooling pond filled to its limit.



1986 Aerial Photo - IMC-NW0 Gypsum Stack

Today our stack consists of 3 active settling areas, with a total of about 230 acres at its top. It is presently about 100 feet high, and requires pumping to reach its top. All dams are rim ditched, and water coverage is excellent. We have never again filled the cooling pond to its limit, and in fact have required make-up water on several occasions.

There is a 4th area of about 50 acres to the north, which we formerly maintained at a low elevation, for emergency gypsum disposal only, so that we could still gravity feed in case of pump failure. However, our pumping system has been sufficiently reliable, that we now use this area preferentially, and plan to incorporate it into the main stack as soon as possible.



Flow Schematic of the IMC-NWO Gypsum Stack

It is important to understand the inter-relationship of the gypsum stack with the cooling pond and plant water balance in general. Many of the decisions we make in managing and operating our gypsum stack are made for the purpose of adjusting/maintaining pondwater balance.

THE GYPSUM'S STACK ROLE IN COOLING

We estimate that at least 15,000 gpm, 10% of our pondwater return, goes with the gypsum to the top of the stack. The gypsum settling ponds can and should be expected to cool this water, before it is decanted and returned to the cooling pond. We have substantiated this fact with temperature profiles and color thermography of our gypsum stack and cooling pond.

ITS ROLE IN PONDWATER BALANCE

The gypsum stack's land area is very significant, perhaps the largest on your site. As such, it is a very important factor in pondwater balance. Its water input to the cooling pond, via rainfall, is well known. Its potential to remove water from the cooling pond system, both passively and actively, may not be as well understood.

Rainfall

Average rainfall at New Wales is about 54 inches per year; our cooling pond's total watershed is made up of the following:

Chemicals Plant	100 acres x .7 runoff coefficient
Cooling Pond	300 acres
Gypsum Stack	430 acres

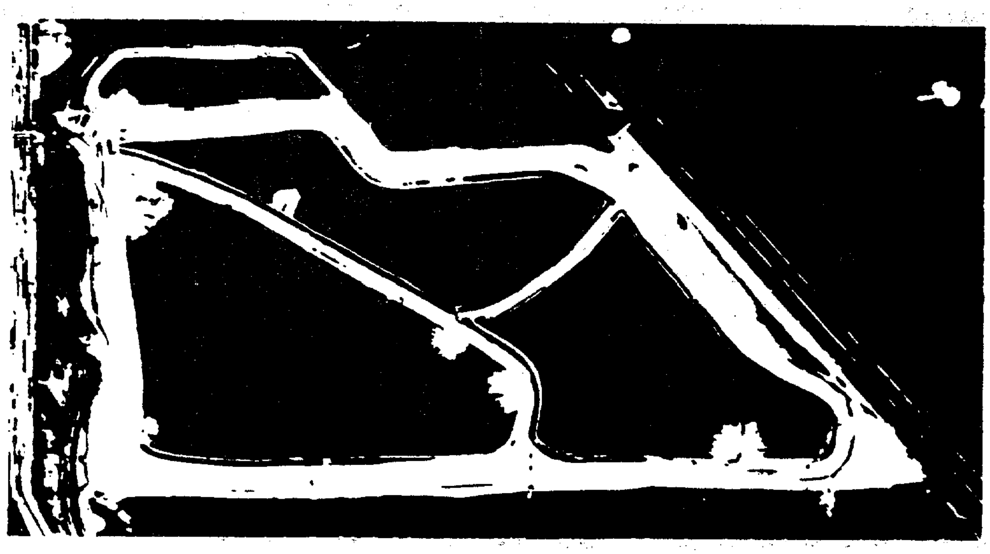
Our gypsum stack's present 430 acre watershed contributes 631 million gallons of water to our cooling pond during an average year.

$$430 \text{ acre} \times \frac{43560 \text{ sq ft}}{\text{acre}} \times \frac{54 \text{ in}}{\text{yr}} \times \frac{\text{ft}}{12 \text{ in}} \times \frac{7.49 \text{ gal}}{\text{cu ft}} = \frac{631 \text{ million gallons}}{\text{year}}$$

Evaporation

The potential to flood the gypsum stack's settling ponds, to maximize water surface and evaporation, and in this way to assist with overall water balance, should be obvious. In "wet" years we can keep 75% of our stack's top area covered with pondwater, and reduce this to less than 20% during "dry" years. Even at 100 ft high, this translates to water coverage on our gypsum ponds from as little as 50 acres to as much as 210 acres.

Gypsum Stack Ponds - Minimizing Evaporation



Gypsum Stack Ponds - Maximizing Evaporation

Assuming lake evaporation rates to be representative, which are about 69 inches per year in Central Florida, evaporation from our gypsum ponds can be adjusted as follows:

from 94 million gallons per year at minimum coverage,
to 394 million gallons per year at maximum coverage

Storing Water ON the Gypsum Stack

The gypsum stack also has tremendous potential to accommodate seasonal weather fluctuations, and even longer term, by manipulating depth and even quantity of the stack ponds.

Our gypsum stack was once operated with as many as 8 settling areas, separated by many crossdams, not all of which were rim-ditched. The dams without rim ditches were very difficult to maintain, and our water coverage was relatively poor - probably 50% at best. We did not inventory our gypsum ponds at that time, but presume that most were relatively shallow, and did not contain very much water.

Our main stack is presently operated with 3 settling areas. Area 4 was just added, and we hope to lift it as quickly as possible and incorporate it into area 1.

We try to operate with a few large areas, because you can store much, much more water than you can in many smaller ones. For example, we have stored over 240 million gallons of water in our largest gypsum pond (at a depth of over 20 ft in its center). The most we have ever stored in the other two combined is 130 million gallons, even though their total area is greater.

We actively manipulate our stack ponds, with respect to both area and depth, to assist with water balance at IMC-NWO. Our gypsum stack ponds have at times contained almost as much water as our cooling pond. Our success is perhaps best demonstrated by the fact that we have never had to treat or release pondwater. In fact, we have at times required make-up water.

Water Stored IN the Gypsum Stack

Water of crystallization in phosphogypsum is widely recognized. But in addition to this, an active gypsum stack may be itself almost half water by volume. If its average dry density is only 75 pcf, and its specific gravity 2.32, it must contain "void" spaces:

$$V \text{ solids} = 75/(62.4 \times 2.32) = .52 = 52\%$$
$$V \text{ voids} = 1 - .52 = .48 = 48\%$$

The "void" spaces in an active gypsum stack are virtually saturated with water. For example, a plant producing 1 million tons of P_2O_5 per year, occupying a volume of 3000 ac-ft, will store 3000 x .48 x 43560 x 7.48 = 470 million gallons of water in its gypsum stack each year.

FORECASTING WATER BALANCE

Our Process Engineering Group has developed a comprehensive computer model of our Cooling Pond, for the purpose of determining and monitoring its performance, both with respect to cooling capacity and water balance. Some of the input and output of this program will be briefly presented here. If you desire more detailed information on this subject, please refer to a paper presented to the AIChE Central Florida Section in March, 1985, by G. M. Hebbard (IMC) and S. J. Babb.

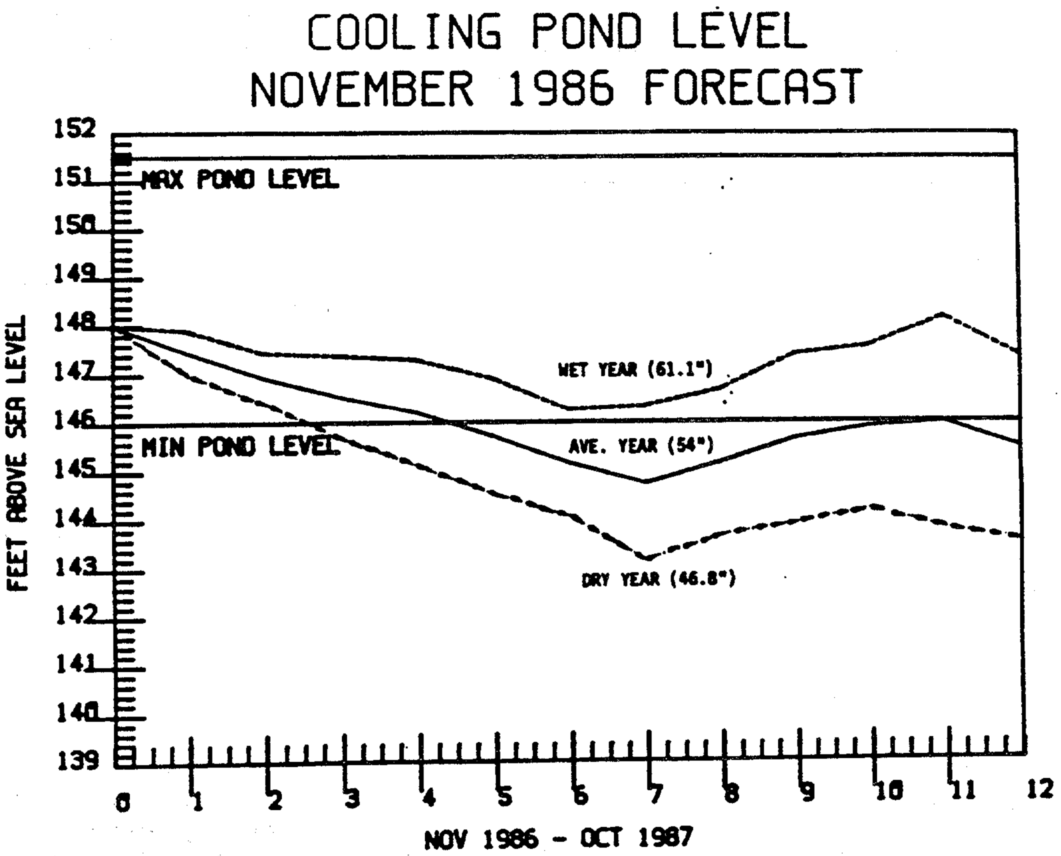
Many weather variables are considered, including rainfall, lake evaporation rates, wind speed, humidity, etc. And of course the appropriate land area for watersheds and water surfaces.

Our ponds are classified as to their status or type as it relates to cooling and/or evaporation. Inactive ponds are available for evaporation; they play a role in water balance, but do not assist with cooling. An example would be gypsum ponds not being used for settling. Active ponds actively participate in cooling, and are further classified into mix flow or plug flow ponds, which exhibit different characteristics with respect to cooling.

Production Rate is another critical element to water balance. The heat load returned with pondwater back to the cooling pond has a tremendous effect on evaporation, and consequently on water balance.

Summary of Input Data: Weather
Watershed
Ponds - Area & Type
Production Rates

The above input is used to predict cooling pond level one year in advance:



These forecasts are updated monthly by our Process Group, and used by Management to make decisions relative to operating the gypsum ponds. Several "as-builts" of cooling pond level have compared very closely with forecasts, when adjusted for actual rainfall, production rates, pondwater inventory, etc.

OPERATING A GYPSUM STACK

This is how we operate the IMC-NWO gypsum stack.

Pumping the Gypsum to the Top of the Stack

As in most of the industry, we take the gypsum cake from the filters and slurry it with pondwater. The slurry is gravity fed from the filters to a surge tank, which discharges directly to the slurry pump(s). A 1000 hp, 21" x 20" ASH GH-9-5 pump, 41" impeller, lifts the slurry to the top of the stack. Pump speed is controlled by surge tank level. Our existing pump has about reached its head capacity, and it is planned to install an in-line booster pump in a few months. This will provide additional discharge head to pump to the 200 ft planned height of our gypsum stack.

This system services all 3 of our phos acid trains, which are each rated at 500,000 tons of phos acid per year. Whether 1 train is operating or 3, we pump about 20,000 gpm - solids may vary from 5% to 20% by weight.

In case of failure of a system component, we have a completely installed spare system - tank, pumps, discharge line, everything.

Transporting the Slurry to the Settling Areas

We are totally committed to the "rim-ditch" method of gypsum stacking at IMC-NWO, as the best way for our gypsum stack to be fully utilized to store and evaporate water and assist in pondwater management.

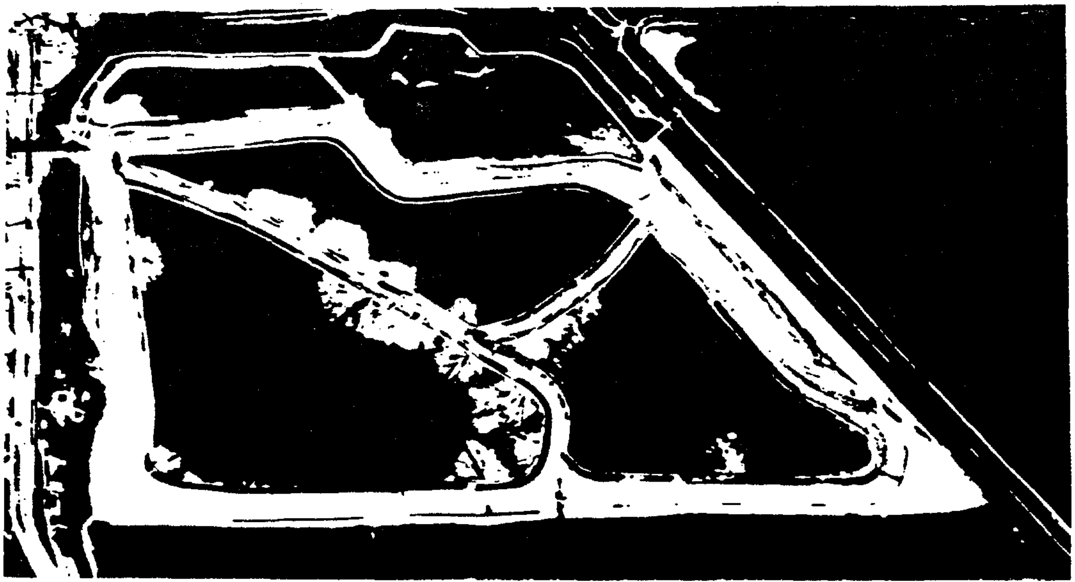
A series of field experiments were conducted several years ago, to better understand the hydraulics of slurry flow in gypsum rim ditches, and to determine the following characteristics:

.014 - .016 roughness coefficient (as used in Manning's equations for open channel flow)
3 - 5 ft/sec transport velocity
.003 - .004 minimum slope to transport the solids

If you have further interest in this research, please contact the authors for a paper presented at the ASCE Florida/South Florida Joint Annual Meeting in 1984, by John Cameron and Ross McGillivray.

Of course the rim ditch, which is excavated to a relatively flat bottom, initially fills with gypsum very rapidly. But eventually sufficient slope is developed in the ditch to attain transport velocity, and the gypsum is conveyed to the settling area. It is important to maintain sufficient flow to keep your velocity in the transport range, which is why we always pump about 20,000 gpm, regardless of how many trains are running. If flow rate is cut, hydraulic radius and velocity will be reduced, perhaps below the minimum required to transport the gypsum.

Whatever area is being used at a given time for settling the gypsum, the slurry is first transported to its furthest reach. Openings are succesively cut through the berm, in about 400 ft increments, until the entire settling area is beached with gypsum along the rim ditch being used.



Settling Areas Filling with Gypsum - the Rim Ditch Way

Decanting Water from the Settling Area

A rim ditch on the opposite side of the active settling area is used to decant water from the settling area, and this and other rim ditches may be used to convey it to the desired point of discharge. A ditch is cut through the perimeter dam, and the decant water drops down the face of the stack, in waterfall fashion, to a perimeter ditch at the toe of the stack. We have culverts at several locations around the stack, to take the water under the toe road and to the cooling pond.

Maintaining the Dams & Ditches

This is the major expenditure in operating the gypsum stack. The rim ditch fills with sedimented gypsum during runs to the settling areas, and needs to be excavated for the next run. And of course the dams/roads, and the berm separating the ditch from the settling area, need to be raised.

Many producers sub-contract this work; we do our own.

We have 2 draglines, Northwest 9570's with 80 ft booms and 3 yard buckets. They work pretty much from dawn to dusk, 7 days a week, less 8 hours each for maintenance. And two bulldozers, 1 D-6 and 1 D-8. These are used intermittently, to level the dams and assist with digging the ditches. Plus a full-time supervisor.

Aside from supervising and directing the activities of the equipment operators, the Gyp Stack Supervisor is constantly inspecting the gypsum stack from stem to stern, from top to bottom. Anything out of the ordinary is reported back to Engineering for investigation.

OPERATING CRITERIA FOR MAINTAINING A GYPSUM STACK

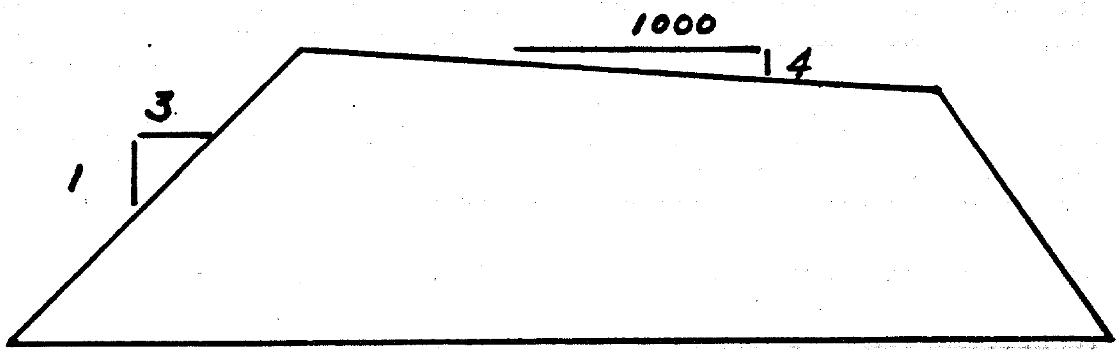
We have done a fairly extensive analysis of the rim ditch method of gypsum stacking, in an effort to minimize digging, maximize productivity, and to properly size the equipment used. For a fairly simple ditch, there is a surprising amount of variables involved:

Overall Stack Slopes - Top & Sides
Quantity of Settling Areas
Roadway/Berm Widths & Slopes
Freeboards & Depths
Crossdams

Overall Stack Slopes - Top & Sides

The top of our stack drops about 25 ft down its longest rim ditch, about 6500 ft, which equates to a slope of almost .004.

The slope across the top of the stack, and in your rim ditches, is essentially self-sustaining. You don't need a survey crew to monitor it. If the slope is excessive, the rim ditch will not be filled with sedimented gypsum at the end of a run, and there will not be as much to dig. If the slope is insufficient, the slurry will over-top the berm between the ditch and the settling area, before the run is completed.



Stack Slopes - Top & Sides

We maintain slopes of 3H+ : 1V on the sides (perimeter face) of the stack. This is essentially a geotechnical consideration, based on the drainage and strength characteristics of the gypsum and foundation soil at your site. Whatever is determined, it can be accomplished incrementally with each lift, or with periodic setbacks, or both. Either way, the amount of material to be moved is the same. We commission an aerial topographic survey about every 18 months, for inventory purposes, and to check the- perimeter slopes on the stack face. If any slopes are found to be too steep, a setback is planned to get them back on course before the next survey.

Regarding "intermediate" slopes, it has been our experience that gypsum will stand on slopes as steep as 1H : 1V, but not for long without sloughing. We strive to maintain intermediate slopes no steeper than 2H : 1V, and to take setbacks as required at least every 20 ft in height.

Quantity of Settling Areas

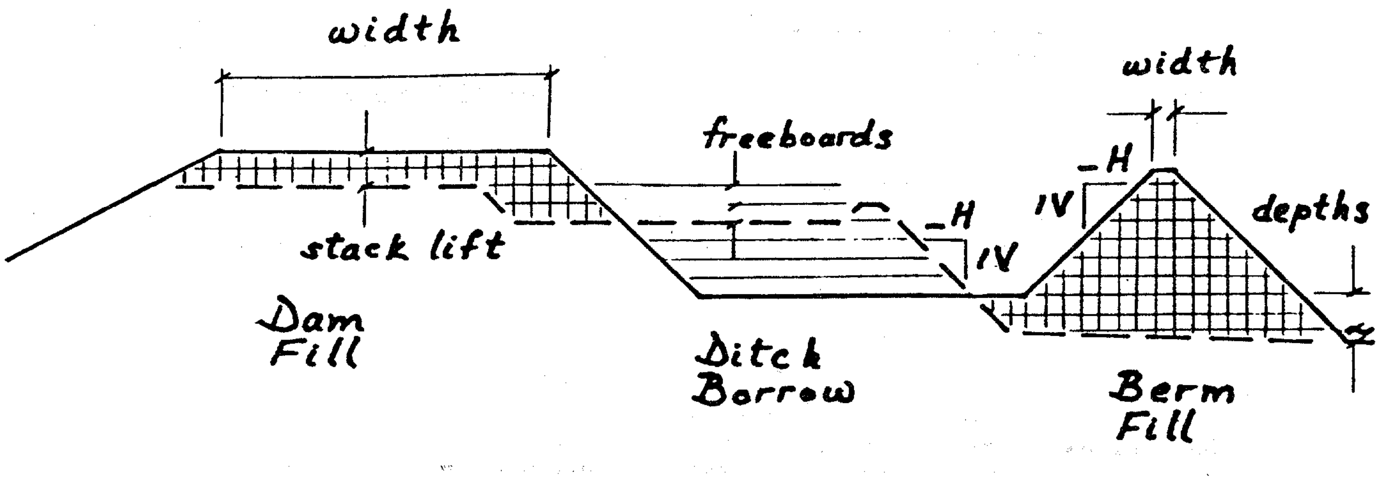
First, how many rim ditches do you need? We use 4 ditches radiating out from the point of introduction of the gypsum slurry. Status of each of the 4 ditches at any given time is as follows:

Ditch 1.	For the current run to a settling area.
Ditch 2.	This should already be dug and ready to go, in case you have a problem with your first one.
Ditch 3.	This is the ditch in which you last ran, and which will now be drying for easy digging.
Ditch 4.	This is the ditch you are currently digging, and should be ready by the time you finish the current run.

Four rim ditches require a minimum of two settling areas. We use 3. More settling areas require more lineal feet of dam and ditch to maintain; but the dams will not be as high, and will not require as much digging (per foot) to maintain. Furthermore, the extra dams are crossdams, which require much less digging than perimeter dams. Overall, our analyses indicate that digging quantity is essentially the same, irrespective of how many settling areas you maintain. Except that your equipment has a lot more ground to cover with many small areas, and while draglines are efficient excavating machines, they are very slow travellers.

Shape of the settling areas is probably more important. Long narrow shapes require much more digging per acre of settling area, than relatively round or square ones.

Another consideration is your ability to store and/or evaporate water. This has already been discussed, and is the primary reason why we went from 8 areas to 3.



Perimeter Dam/Ditch Cross-Section

The above cross-section will be used to develop the other operating criteria which we consider when digging our rim ditches and building our dams and berms.

Roadway/Berm Widths & Slopes

Our operating philosophy for both of these is to use the minimum necessary to assure the safety of our equipment and personnel.

Our draglines require about 30 foot of road on which to operate. We continue to have success with berms as narrow as 2 foot at the top. They do blow out on occasion, but we always have another ditch in which to run in that eventuality.

We maintain slopes of essentially 1.5H : 1V on the sides of the roads and probably 1H : 1V on the berms, as steep as the gypsum will stand.

Freeboards & Depths

The primary consideration is to ensure that if the rim ditch should overflow, that it overflow the berm into the settling area, and not the dam/road. For purposes of digging analysis, freeboards can be handled separately as follows:

Dam (Road) to Ditch - we use .5 foot
Berm to Ditch - also .5 foot

We try to maintain our dam & ditch elevations sufficiently above that of the settling area, so that we have to dig no deeper than 1' above the water line, to get sufficient material out of the ditch with which to raise the road and berm. Otherwise we would end up digging soup, which drastically reduces productivity.

As to water depth, this refers to the minimum water depth which you wish to maintain at the rim of the settling area, to insure maximum water coverage for evaporation and water balace purposes. We strive for zero.

Crossdams

Crossdams require much less digging than perimeter dams. It need not step in like a perimeter dam; it can go straight up. Also, if you are as committed to rim ditching as we are, you have material from two ditches, one on each side, with which to build it. Consequently, crossdam ditches need not be nearly as wide as perimeter ditches. The dams themselves do need to be as wide, if you wish to use the same equipment as that used to construct your perimeter dams.

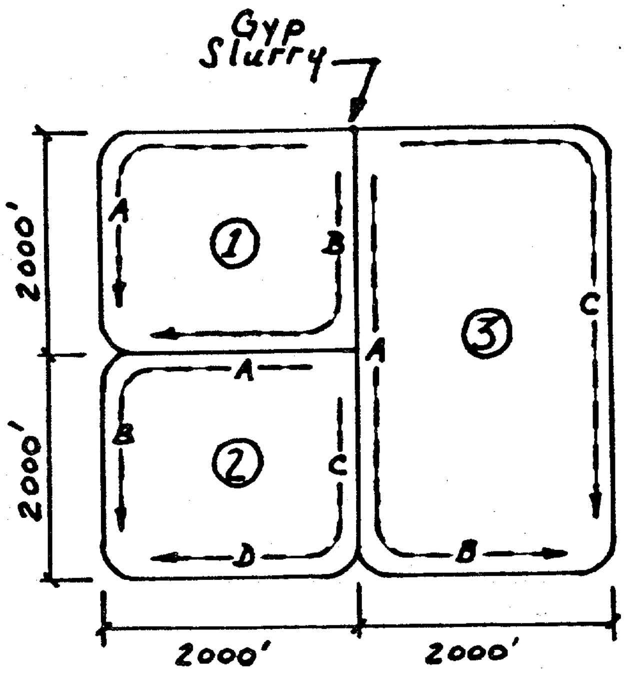
Quantifying Rim Ditch Digging & Maintenance

Summarizing the above variables, we have the following input:

Slope across Stack (ft per 1000 ft)		"xb" =	4
Dam Slopes:	Stack face (_H : 1V)	"xc" =	3
	Roads (_H : 1V)	"xd" =	1.5
	Berms (_H : 1V)	"xe" =	1
Dam Widths:	Perimeter road (ft)	"xf" =	30
	Cross road (ft)	"xg" =	30
	Berm (ft)	"xh" =	2
Freeboards:	Dam to Berm (ft)	"xi" =	0.5
	Berm to Ditch (ft)	"xj" =	0.5
	Min. Dry Dig (ft)	"xk" =	1
	Min. Water Depth (ft)	"xl" =	0

Add to these your actual stack geometry (area and rim ditch lengths for each settling area), and you can quantify how much fill material is required to raise your dams and berms for a typical stack lift; and what ditch width will provide sufficient borrow material.

We have developed a computer program to quantify the rim ditch digging required for dam/berm maintenance. A sample run is contained in the Appendix for the following configuration:



Sample Configuration for a Gypsum Stack

For this configuration, it is calculated that 122,000 cubic yards of ditch will be dug for a 2 foot stack lift. This represents 10.3% of the 736 acre-feet of gypsum that will be deposited for the given lift. That can be a lot of digging over a year's time, especially when you consider that the gypsum in the rim ditch is freshly sedimented and not yet consolidated to your average stack density.

Such a computer program can also be used to forecast what your dig will be from year to year as your stack geometry changes with height, and help you to budget for possible manpower and equipment changes. And you can evaluate possible changes in configuration, or other variables that may be within your control, to optimize your gypsum stacking operation.

Dragline Reach

This can be another useful output of a computerized program. You do not wish to create a set of conditions beyond the reach of your equipment, at least not without forewarning. Some dams and berms may be constructed with bulldozers pushing up from within the ditch, especially where the ditch is high and dry. But most of this work is done by draglines, which do have a limited reach.

STORAGE REQUIREMENTS FOR GYPSUM

P205 is produced by weight, but gypsum stacks grow in space. We estimate a disposal requirement of 3000 ac-ft of gypsum pile per million tons of P205 production. We arrived at this estimate as follows:

Calculating the Storage Requirement

For Gypsum : P205 Ratio, we assume 5 : 1, by weight. Even with some rather sophisticated mass balance calculations, it is surprisingly difficult to get a precise figure for this ratio. The true figure is probably somewhere between 4.75 and 5.25 : 1.

Actual core samples of our stack, taken several years ago, yielded dry densities ranging from 60 to 90 pcf for our gypsum stack. We use 75 pcf as an average.

Per million tons of P205 production, this equates to

$$5{,}000{,}000 \text{ tons} \times \frac{2000 \text{ lbs}}{\text{ton}} \times \frac{\text{cu ft}}{75 \text{ lbs}} \times \frac{\text{acre}}{43560 \text{ sq ft}} = 3061 \text{ acre-ft gypsum}$$

Measuring the Storage Requirement

From periodic aerial topographic surveys of our gypsum stack, we calculate and compare volume changes against P205 production for the same period.

Results of these have been as variable as those above, ranging from 2000 to 4400 ac-ft of gypsum per million tons of P205. Our last survey indicated an overall disposal requirement of 2990 ac-ft of gypsum per million tons of P205, for the last 7.5 million tons of P205 produced at IMC-NWO.

LAND PLANNING FOR GYSUM STACKS

Long range planning is required to provide for your gypsum disposal needs. Following are some factors we consider:

How Much Disposal Volume
How High & How Big
Checking for Storm Surge Capacity
Checking for Water Balance

How Much Disposal Volume

Ideally, you should be planning for the life of your facility, perhaps 50 years. And you need to forecast production rates, including any expansions which may be planned for the future. However, considering cost of land preparation, water balance, etc., it is probably not realistic to provide for this much gypsum stack at start-up.

On the other hand, the time and money invested to just design and obtain permitting for a gypsum stack expansion can be very considerable, in addition to that required for whatever land preparation and other facility improvements may be involved. We are presently designing for a 20 year gypsum stack expansion, to be implemented in two phases.

For whatever term and rates you select, it is a simple calculation to quantify total P2O5 production and gypsum disposal volume for which you need to provide; assuming of course that you can relate one to the other.

How High & How Big

A lot of factors may need to be evaluated in order to make this decision.

Height limitations
Quantity & minimum size of settling areas
Side slopes
Can it be placed adjacent to an existing stack
Economics of "vertical vs "horizontal" stacking

Height limitations: Pumping head capacity/feasibility; geotechnical considerations may well be the primary factor in this regard.

Quantity and minimum size of settling areas. Whatever height is selected, check to see that you are comfortable with its projected area at the top, in view of your production rates.

Side slopes may greatly affect volume available for disposal. Flatter slopes, especially on long faces, can drastically reduce disposal area as the stack increases in height.

If you are considering a stack expansion, can it be placed against an existing one? If the expansion's longest side can be placed against an existing stack, very little volume will be lost due to side slopes.

And of course economics - operating/capital cost of "vertical" expansion vs. "horizontal" expansion.

Checking for Storm Surge Capacity

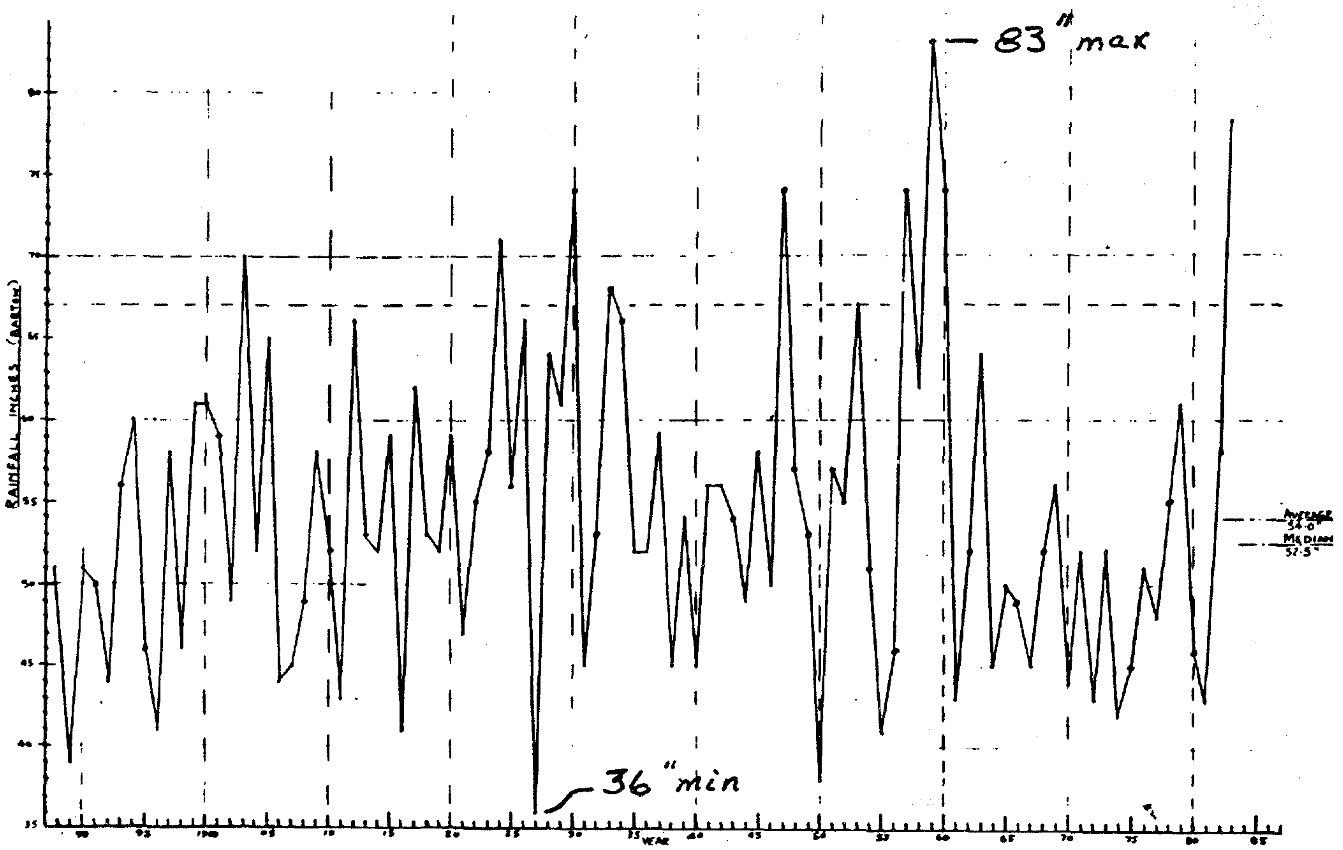
We design for a 100 year storm; at our location, that's 12 inches in 24 hours. We check to insure that our cooling ponds at grade can accept and/or discharge this rainfall from their total watershed - on 800 acres, that comes to 261 million gallons. We do not rely on the gypsum ponds or any other elevated ponds to take on additional water. They are presumed to be unavailable and possibly overflowing, with all power and pumps down for the duration of the storm.

If your ponds at grade can not handle this kind of "instantaneous" storm surge, you may wish to re-evaluate the size of your proposed gypsum stack, the balance between your elevated ponds and those at grade, and/or inactive stacks which may be reclaimed and removed from the watershed.

Checking for Water Balance

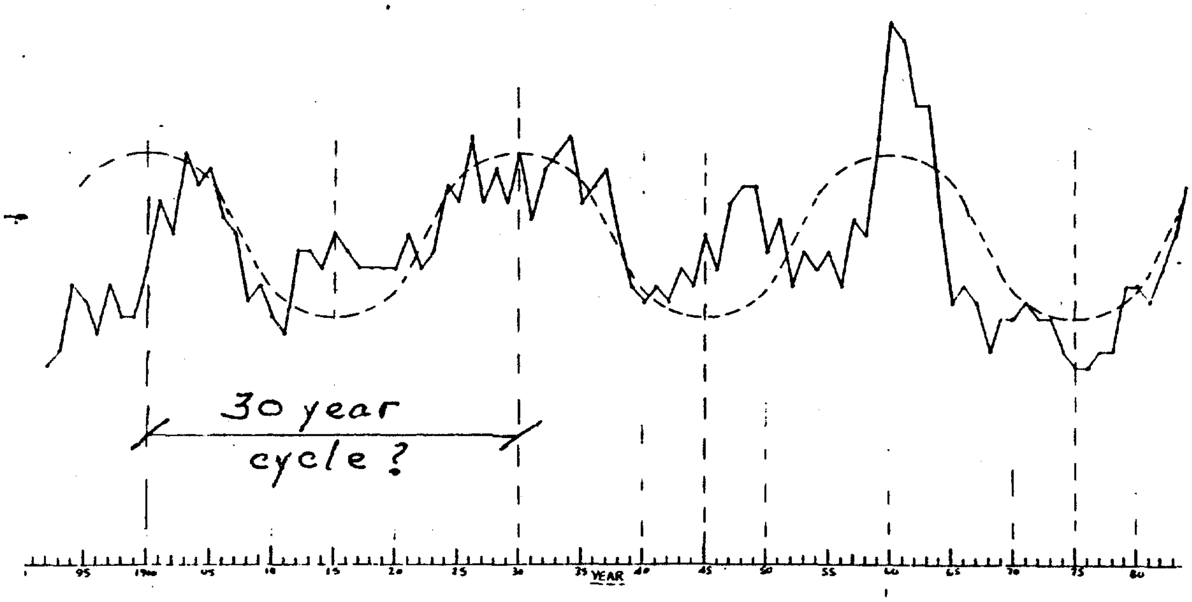
Short-term you should be looking for a favorable balance between rainfall/watershed and evaporation/water surface/production heat load, at least for the seasonal variations which are likely to occur during an average year.

Unfortunately, more often than not, weather does not occur in averages. For example, consider actual recorded rainfall at Bartow, Florida, which is about 10 miles from our facility:



Actual Annual Rainfall at Bartow, Florida, 1888-1983

We plotted a series of rolling averages, to see if there might be some long-term rainfall patterns for which we could design surge capacity into our gypsum stack/cooling pond system.



Annual Rainfall at Bartow, 5 year Rolling Average

We think we see a pattern in this plot, occurring in 30 year cycles. We therefor developed another computer program to analyze a proposed gypsum stack/cooling pond system for long-term water balance. This program takes the projected cooling pond level output from the cooling pond model, month by month, for an average year. Adjusted by "real" rainfall month by month, selected from some past historical period, this will hopefully more accurately predict the future.

The model can be programmed to accept make-up water whenever predicted level falls below the cooling pond's minimum operating level, and to overflow whenever it rises above maximum operating level. Overflow pondwater could be collected in an "emergency holding pond", and treated and discharged, or returned to the cooling pond when possible. The projected cost of water treatment should be annualized and added to operating costs for the particular system being analyzed.

It should be noted that rainfall is not the only variable which affects water balance, but we believe it to be the principal one, and the only one we have considered so far.

ACKNOWLEDGEMENTS

We wish to acknowledge contributions from the following personnel at IMC-New Wales Operations, who helped us to understand how the gypsum stack really works, and in other ways assisted with preparation of this paper.

D. D. Freeman	J. G. Peters
G. M. Hebbard	R. D. Raburn
D. E. Hirsch	J. J. Yarnell
A. L. Hopper	

GYP STACK RIM DITCH ANALYSIS #1 PAGE 1 - 1

DITCH DETAIL - AREA #1

STATION (FT)	BERM HT (FT)	DAM LIFT	+	BERM LIFT	=	TOTAL DIG (CF/LF)	DRY DIG MAX D (FT	X	MIN W FT)	DRAG LINE REACH (FT)
100	18.1	78	+	136	=	214	16	X	33	63
300	17.3	78	+	129	=	207	15	X	32	62
500	16.5	78	+	123	=	201	14	X	32	62
700	15.7	78	+	117	=	195	13	X	31	61
900	14.9	78	+	110	=	188	12	X	31	61
1100	14.1	78	+	104	=	182	12	X	30	60
1300	13.3	78	+	97	=	175	11	X	30	60
1500	12.5	78	+	91	=	169	10	X	29	59
1700	11.7	78	+	85	=	163	9	X	29	59
1900	10.9	78	+	78	=	156	8	X	29	59
2100	10.1	78	+	72	=	150	8	X	29	59
2300	9.3	78	+	65	=	143	7	X	29	59
2500	8.5	78	+	59	=	137	6	X	30	60
2700	7.7	78	+	53	=	131	5	X	31	61
2900	6.9	78	+	46	=	124	4	X	34	64
3100	6.1	78	+	40	=	118	4	X	37	67
3300	5.3	78	+	33	=	111	3	X	43	73
3500	4.5	78	+	27	=	105	2	X	55	85
3700	3.7	78	+	21	=	99	1	X	83	113
3900	3.5	78	+	19	=	97	1	X	97	127
		-----		-----		-----				
TOTAL DITCH #1A - TYPE P		11556	+	11147			= 22702 (CY)			
100	18.1	36	+	41	=	77	16	X	24	48
300	17.3	36	+	40	=	76	15	X	24	48
500	16.5	36	+	38	=	74	14	X	23	47
700	15.7	36	+	36	=	72	13	X	22	46
900	14.9	36	+	35	=	71	12	X	21	45
1100	14.1	36	+	33	=	69	12	X	20	44
1300	13.3	36	+	32	=	68	11	X	20	44
1500	12.5	36	+	30	=	66	10	X	19	43
1700	11.7	36	+	28	=	64	9	X	19	43
1900	10.9	36	+	27	=	63	8	X	18	42
2100	10.1	36	+	25	=	61	8	X	18	42
2300	9.3	36	+	24	=	60	7	X	17	41
2500	8.5	36	+	22	=	58	6	X	17	41
2700	7.7	36	+	20	=	56	5	X	17	41
2900	6.9	36	+	19	=	55	4	X	18	42
3100	6.1	36	+	17	=	53	4	X	19	43
3300	5.3	36	+	16	=	52	3	X	22	46
3500	4.5	36	+	14	=	50	2	X	28	52
3700	3.7	36	+	12	=	48	1	X	42	66
3900	3.5	36	+	12	=	48	1	X	49	73
		-----		-----		-----				
TOTAL DITCH #1B - TYPE X		5333	+	3861	=	9194 (CY)				

APPENDIX

Computer print-out of a sample "Rim Ditch Dig Analysis"

```
GYP STACK RIM DITCH ANALYSIS #1          PAGE 1 - S

STACK SUMMARY
-------------
AREA           AREA          PERIMETER      TOTAL DIG      DIG AS %
#              (AC)          (FT)           (CY)           STORAGE

1               92            8000           31896          10.7
2               92            8000           28367          9.6
3               184           12000          61701          10.4
                ---           -----          ------         ----
TOTAL STACK     368           28000          121964         10.3

AREA DETAIL / DITCH SUMMARY
---------------------------
DITCH    TYPE  LENGTH        DAM LIFT       BERM LIFT      TOTAL DIG
#       X OR P (FT)          (CY)           (CY)           (CY)

1A         P     4000         11556          11147          22702
1B         X     4000         5333           3861           9194
               -----         ------         ------         ------
TOTAL AREA #1  8000           16889          15007          31896

2A         X     2000        2667           2519           5185
2B         P     2000        5778           3221           8999
2C         X     2000        2667           2519           5185
2D         P     2000        5778           3221           8999
               -----         ------         ------         ------
TOTAL AREA #2  8000           16889          11479          28367

3A         X     4000        5333           6222           11556
3B         P     2000        5778           3221           8999
3C         P     6000         17333         23813          41147
               -----         ------         ------         ------
TOTAL AREA #3  12000          28444          33256          61701
```

GYP STACK RIM DITCH ANALYSIS #1 PAGE 1 - 2

DITCH DETAIL - AREA #2

STATION (FT)	BERM HT (FT)	DAM LIFT	+	BERM LIFT	=	TOTAL DIG (CF/LF)	DRY DIG MAX D (FT	X X	MIN W FT)	DRAG LINE REACH (FT)
2100	18.1	36	+	41	=	77	16	X	24	48
2300	17.3	36	+	40	=	76	15	X	24	48
2500	16.5	36	+	38	=	74	14	X	23	47
2700	15.7	36	+	36	=	72	13	X	22	46
2900	14.9	36	+	35	=	71	12	X	21	45
3100	14.1	36	+	33	=	69	12	X	20	44
3300	13.3	36	+	32	=	68	11	X	20	44
3500	12.5	36	+	30	=	66	10	X	19	43
3700	11.7	36	+	28	=	64	9	X	19	43
3900	10.9	36	+	27	=	63	8	X	18	42
TOTAL DITCH #2A - TYPE X		2667	+	2519	=	5185 (CY)				
4100	10.1	78	+	72	=	150	8	X	29	59
4300	9.3	78	+	65	=	143	7	X	29	59
4500	8.5	78	+	59	=	137	6	X	30	60
4700	7.7	78	+	53	=	131	5	X	31	61
4900	6.9	78	+	46	=	124	4	X	34	64
5100	6.1	78	+	40	=	118	4	X	37	67
5300	5.3	78	+	33	=	111	3	X	43	73
5500	4.5	78	+	27	=	105	2	X	55	85
5700	3.7	78	+	21	=	99	1	X	83	113
5900	3.5	78	+	19	=	97	1	X	97	127
TOTAL DITCH #2B - TYPE P		5778	+	3221	=	8999 (CY)				
2100	18.1	36	+	41	=	77	16	X	24	48
2300	17.3	36	+	40	=	76	15	X	24	48
2500	16.5	36	+	38	=	74	14	X	23	47
2700	15.7	36	+	36	=	72	13	X	22	46
2900	14.9	36	+	35	=	71	12	X	21	45
3100	14.1	36	+	33	=	69	12	X	20	44
3300	13.3	36	+	32	=	68	11	X	20	44
3500	12.5	36	+	30	=	66	10	X	19	43
3700	11.7	36	+	28	=	64	9	X	19	43
3900	10.9	36	+	27	=	63	8	X	18	42
TOTAL DITCH #2C - TYPE X		2667	+	2519	=	5185 (CY)				
4100	10.1	78	+	72	=	150	8	X	29	59
4300	9.3	78	+	65	=	143	7	X	29	59
4500	8.5	78	+	59	=	137	6	X	30	60
4700	7.7	78	+	53	=	131	5	X	31	61
4900	6.9	78	+	46	=	124	4	X	34	64
5100	6.1	78	+	40	=	118	4	X	37	67
5300	5.3	78	+	33	=	111	3	X	43	73
5500	4.5	78	+	27	=	105	2	X	55	85
5700	3.7	78	+	21	=	99	1	X	83	113
5900	3.5	78	+	19	=	97	1	X	97	127
TOTAL DITCH #2D - TYPE P		5778	+	3221	=	8999 (CY)				

DITCH DETAIL AREA #3

STATION (FT)	BERM HT (FT)	DAM LIFT	+	BERM LIFT	=	TOTAL DIG (CF/LF)	DRY DIG MAX D (FT	X	MIN W FT)	DRAG LINE REACH (FT)
100	26.1	36	+	57	=	93	24	X	33	57
300	25.3	36	+	56	=	92	23	X	33	57
500	24.5	36	+	54	=	90	22	X	32	56
700	23.7	36	+	52	=	88	21	X	31	55
900	22.9	36	+	51	=	87	20	X	30	54
1100	22.1	36	+	49	=	85	20	X	29	53
1300	21.3	36	+	48	=	84	19	X	28	52
1500	20.5	36	+	46	=	82	18	X	27	51
1700	19.7	36	+	44	=	80	17	X	26	50
1900	18.9	36	+	43	=	79	16	X	25	49
2100	18.1	36	+	41	=	77	16	X	24	48
2300	17.3	36	+	40	=	76	15	X	24	48
2500	16.5	36	+	38	=	74	14	X	23	47
2700	15.7	36	+	36	=	72	13	X	22	46
2900	14.9	36	+	35	=	71	12	X	21	45
3100	14.1	36	+	33	=	69	12	X	20	44
3300	13.3	36	+	32	=	68	11	X	20	44
3500	12.5	36	+	30	=	66	10	X	19	43
3700	11.7	36	+	28	=	64	9	X	19	43
3900	10.9	36	+	27	=	63	8	X	18	42
		-----		-----		-----				
TOTAL DITCH #3A - TYPE X		5333	+	6222	=	11556 (CY)				
4100	10.1	78	+	72	=	150	8	X	29	59
4300	9.3	78	+	65	=	143	7	X	29	59
4500	8.5	78	+	59	=	137	6	X	30	60
4700	7.7	78	+	53	=	131	5	X	31	61
4900	6.9	78	+	46	=	124	4	X	34	64
5100	6.1	78	+	40	=	118	4	X	37	67
5300	5.3	78	+	33	=	111	3	X	43	73
5500	4.5	78	+	27	=	105	2	X	55	95
5700	3.7	78	+	21	=	99	1	X	83	113
5900	3.5	78	+	19	=	97	1	X	97	127
		-----		-----		-----				
TOTAL DITCH #3B - TYPE P		5778	+	3221	=	8999 (CY)				
100	26.1	78	+	200	=	278	24	X	41	71
300	25.3	78	+	193	=	271	23	X	40	70
500	24.5	78	+	187	=	265	22	X	40	70
700	23.7	78	+	181	=	259	21	X	39	69
900	22.9	78	+	174	=	252	20	X	38	68
1100	22.1	78	+	168	=	246	20	X	37	67
1300	21.3	78	+	161	=	239	19	X	36	66
1500	20.5	78	+	155	=	233	18	X	35	65
1700	19.7	78	+	149	=	227	17	X	35	65
1900	18.9	78	+	142	=	220	16	X	34	64
2100	18.1	78	+	136	=	214	16	X	33	63
2300	17.3	78	+	129	=	207	15	X	32	62
2500	16.5	78	+	123	=	201	14	X	32	62
2700	15.7	78	+	117	=	195	13	X	31	61
2900	14.9	78	+	110	=	188	12	X	31	61
3100	14.1	78	+	104	=	182	12	X	30	60
3300	13.3	78	+	97	=	175	11	X	30	60
3500	12.5	78	+	91	=	169	10	X	29	59
3700	11.7	78	+	85	=	163	9	X	29	59
3900	10.9	78	+	78	=	156	8	X	29	59
4100	10.1	78	+	72	=	150	8	X	29	59
4300	9.3	78	+	65	=	143	7	X	29	59
4500	8.5	78	+	59	=	137	6	X	30	60
4700	7.7	78	+	53	=	131	5	X	31	61
4900	6.9	78	+	46	=	124	4	X	34	64
5100	6.1	78	+	40	=	118	4	X	37	67
5300	5.3	78	+	33	=	111	3	X	43	73
5500	4.5	78	+	27	=	105	2	X	55	95
5700	3.7	78	+	21	=	99	1	X	83	113
5900	3.5	78	+	19	=	97	1	X	97	127
		-----		-----		-----				
TOTAL DITCH #3C - TYPE P		17333	+	23813			= 41147 (CY)			

IMPLICATIONS OF PHOSPHOGYPSUM ENGINEERING PROPERTIES ON GYPSUM STACK MANAGEMENT AND RECLAMATION

by

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ABSTRACT

The engineering properties of phosphogypsum have major implications on the management and reclamation of gypsum stacks. Engineering properties of interest with regard to gypsum stack management and reclamation include: settling and sedimentation characteristics for sizing retention areas; in situ density and moisture content for material and water balance; permeability and field capacity characteristics for flow analyses, gypsum handling and drainage; compressibility, consolidation, and creep properties for settlement and deformation evaluations; shear strength properties for stability analyses; and leaching/solubility characteristics for post-reclamation water balance and leachate treatment. Typical values of engineering properties measured both in the laboratory and in situ on phosphogypsum produced at 21 facilities both in the United States and abroad are presented. The effects of crystal morphology and aging on in situ density, compressibility, long-term creep behavior and cementation are discussed. Examples are also presented illustrating the effects of engineering properties on management and reclamation methods applied to new and existing facilities.

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SOIL AMENDMENT

AMELIORATION OF ACID SUBSOILS WITH PHOSPHOGYPSUM

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ABSTRACT

Highly weathered acid subsoils often limit root penetration of crops because of the unfavorable conditions such as high and low levels of soluble Al and Ca respectively. The absence of roots in subsoil horizons results in lower yields because of the crop's inability to extract water often the primary yield limiting factor in many soils. Usually economics preclude the incorporation limestone to depth in the soil profile but phosphogypsum being more soluble can be applied to the surface and slowly move down. Significant yield responses (25-50%) to gypsum application have been recorded in a number of highly weathered acid soil profiles with crops such as maize soybeans, and alfalfa. Gypsum readily supplies the subsoil with Ca, promoting root elongation and in addition reduces the level of soluble Al which is toxic. This ameliorative effect allows deeper root penetration with attendant improved water extraction resulting in yield increases. The possible mechanisms for this amelioration are complexation of Al^{3+} with $SO_4{}^{2-}$ as the ion pair $AlSO^{4+}$, exchange of $SO_4{}^{2-}$ for solid phase OH^- resulting in the formation of $AlOH^{2+}$ and $Al(OH)_2{}^+$ complexes, mineral precipitation such as alunite or basaluminite and ionic strength induced adsorption.

INTRODUCTION

Acid subsoils usually prevent the penetration of the roots of sensitive crops beyond the topsoil with the consequence that water stored in the subsoil is beyond their reach which, in turn, limits productivity particularly during dry spells. For roots to proliferate in subsoils, adequate levels of soluble Ca must be present and soluble Al must be low enough not to interfere with the metabolic activity of roots. Usually acid subsoils do not meet these requirements.

The beneficial effect of gypsum on the amelioration of acid subsoils was originally demonstrated by Reeve and Sumner (1972) and Sumner (1970) while in a recent review by Sumner et al. (1986), these findings were further corroborated and in addition illustrated other benefits of phosphogypsum such as improved infiltration and reduced dispersion and crust formation in highly weathered soils. Normally liming is the strategy used to neutralize acid soils but unfortunately this approach is limited to topsoils because lime moves extremely slowly if at all down the soil profile. On the other hand, phosphogypsum being fairly soluble readily moves into the subsoil where it can effect amelioration. In addition to its beneficial effects on subsoil acidity, phosphogypsum is likely to further promote the growth of crops by virture of its residual P content (0.6-1% P_2O_5). In recent years substantial quantities of gypsum, being a by-product of the phosphoric acid industry, have been accumulating to such an extent that now disposal has become a problem. The objective of this paper is to present a case supporting the use of phosphogypsum as a potential ameliorant for acid subsoils which are currently seriously limiting crop production in many parts of the world.

MATERIALS AND METHODS

Field experiments were conducted at four locations, three in Georgia and one in South Africa. Details of the soil series studied and treatments applied are presented below for each experiment.

EXPERIMENT 1 (GEORGIA)

This experiment was commenced in 1981 on an Appling sandy loam (clayey, kaolinitic, thermic Typic Hapludult) with the following treatments: (a) control in which no chemical or physical alteration was made to the subsoil: (b) gypsum where 35 tons ha^{-1} was incorporated into the topsoil; (c) mixed and limed in which the profile was excavated and mixed with a backhoe to a depth of lm after removal of topsoil with sufficient lime added to each 0.15 m layer to neutralize exchangeable Al amounting to a total of 35 ton ha^{-1}. Topsoils on each plot received the same fertilizer and lime as required by soil test. The experiment was replicated three times. In 1981 and 1982 soybeans were grown while in 1983 maize for silage was planted.

EXPERIMENT 2 (GEORGIA)

In 1982 a second experiment was initiated on another Appling sandy loam utilizing alfalfa as the test crop. The treatments and management were essentially the same as in Experiment 1 with the exception that only 10 tons gypsum ha^{-1} was applied.

EXPERIMENT 3 (SOUTH AFRICA)

This experiment on a Normandien clay loam (clayey, kaolinitic, thermic, Plinthic Paleudult) was commenced in 1983 with maize as the test crop with essentially the same types of treatment as in Experiment 2. The major difference was in the deep lime treatment where 10 ton dolomitic lime ha^{-1} was incorporated below the plow layer with a Wye-double-digger.

EXPERIMENT 4 (GEORGIA)

This experiment, commenced in 1984, was conducted on a Tifton loamy sand (fine-loamy, siliceous, thermic, Plintic Paleudult) with alfalfa as the test crop. The treatments were essentially the same as in Experiment 2 with the addition of two further rates of gypsum and the two way splitting of all main plots to accommodate two levels of Mg (0 and 100 kg ha^{-1}) and four levels of K (0, 125, 250, 375 kg ha^{-1}).

SAMPLING

Soil samples (both topsoil and subsoil by 0.15 m depth interval) were taken on all experiments at various times. Root sampling was conducted separately on Experiments 2 and

3. Tissue samples were taken for analysis from all crops on all experiments.

ANALYSES

Soils were analysed by well accepted standard methods such as extraction with M NH_4OAc for exchangeable cations, extraction with M KCl for exchangeable Al and H, pH in water. Activities of ions in the soil solution were calculated from concentrations in soil solution (Debye-Huckel) extracted by centrifugation at field capacity. Roots were extracted from soil using a Gillison root washing apparatus. Plant tissue was analysed by emission spectrograph after dry ashing and dissolution in HCl. Soil moisture was measured with a neutron moisture meter.

RESULTS AND DISCUSSION

EXPERIMENT 1

The effect of subsoil treatments on yield of soybeans and maize is presented in Table I. The mixed and limed treatment represents the yield that can be attained when the

Table I. Effect of subsoil amendment on soybean and maize yield on an Appling sandy loam (Data of Hammel, Sumner and Shahandeh (1985)

Treatment	Soybean Grain 1981	 1982	Maize Silage 1983
		metric tons ha^{-1}	
Control	0.941(100)[†]	1.283(100)	26.2(100)
Gypsum	1.216(129)	1.613(126)	35.4(135)
Mixed & Limed	1.761(187)	2.007(156)	41.0(156)
$LSD_{0.05}$	0.304(32)	0.223(17)	5.4(21)

[†] Expressed as a percentage of the control.

major limiting factor to root penetration of the subsoil (toxic level of Al) has been eliminated. In the first year, no significant response to gypsum was obtained because insufficient time had elapsed to allow the gypsum to move into the subsoil. In subsequent years, highly significant yield responses to gypsum were obtained indicating the potential ameliorating effect that gypsum might have on highly weathered acid subsoils. The reasons for these yield responses are to be found in Table II. In the control treatment, exchangeable Ca rapidly decreases with depth while the reverse is true for exchangeable Al. Deep liming increases exchangeable Ca to nearly uniform levels down the profile while reducing exchangeable Al to virtually zero. With time, gypsum treatment results in increased Ca and decreased Al down the profile but to an extent considerably less than brought about by deep liming. Gypsum treatment had no effect on soil pH in M KCl (data not presented).

Table II. Effect of subsoil treatments on exchangeable cations in an Appling profile with time. (Data of Hammel, Sumner and Shahandeh (1985))

Depth m	Exchangeable					
	Ca			Al		
	1981	1982	1983	1981	1982	1983
	cmol(+) kg^{-1}					
	Control					
0-0.15	6.24	6.01	-	0.20	0.21	-
0.15-0.30	1.39	1.45	-	1.31	1.44	-
0.30-0.45	0.95	0.96	-	1.70	1.50	-
0.45-0.60	0.56	0.53	-	2.01	1.96	-
0.60-0.75	0.35	0.40	-	2.43	2.61	-
0.75-0.90	0.22	0.29	-	2.52	2.35	-
	Gypsum					
0-0.15	21.30	18.72	10.40	0.00	0.01	0.02
0.15-0.30	5.00	3.19	3.70	1.14	1.13	0.90
0.30-0.45	1.21	2.08	3.30	1.92	1.46	0.92
0.45-0.60	0.68	1.09	2.98	2.28	2.35	1.05
0.60-0.75	0.44	0.74	2.30	2.55	2.70	1.51
0.75-0.90	0.30	0.52	1.91	2.88	2.92	1.76
	Mixed and Limed					
0-0.15	5.47	4.62	-	0.00	0.01	-
0.15-0.30	3.58	3.36	-	0.00	0.18	-
0.30-0.45	3.29	2.68	-	0.00	0.28	-
0.45-0.60	4.41	2.80	-	0.00	0.26	-
0.60-0.75	4.04	3.59	-	0.00	0.15	-
0.75-0.90	4.43	3.87	-	0.00	0.00	-

Nevertheless there was sufficient amelioration of the profile to allow increased root penetration as evidenced by the water removal pattern and leaf water potentials (Table III). Both gypsum and deep liming increased water removal over control down the profile indicating that rooting with depth was promoted by both treatments. This increased water availability is also reflected in the leaf water potentials which show a less stressed condition of plants in the ameliorated profiles resulting in greater biomass production.

Table III. Effect of subsoil treatments on water removal by soybeans from an Appling profile and leaf water potential measuring during a 10 day period in 1982 (Data of Hammel, Sumner and Shahandeh (1985))

Depth	Control		Gypsum		Mixed and Limed	
m	Water removed	Leaf water potential	Water removed	Leaf water potential	Water removed	Leaf water potential
	mm m^{-1}	bars	mm m^{-1}	bars	mm m^{-1}	bars
0-0.15	20	-14.0	50	-9.3	70	-7.3
0.15-0.30	10		40		70	
0.30-0.45	10		30		80	
0.45-0.60	10		30		80	
0.60-0.75	10		40		80	
0.75-0.90	10		20		80	
0.90-1.05	10		20		90	
Total	80		180		550	

EXPERIMENT 2

Based on the experiences of the first experiment a second with alfalfa was initiated in 1982 to evaluate the performance of a valuable perennial crop. Yield response patterns are presented in Table IV. Again little yield response to gypsum was obtained in the first year but subsequently highly significant yield responses were obtained over the next four years in some years closely approaching the yield level on the mixed and limed treatment.

Table IV. Effect of subsoil amendment on alfalfa yield on an Appling sandy loam (Data of Sumner et al. (1986))

Treatment	1982	1983	1984	1985	1986
			Alfalfa Hay metric tons ha^{-1}		
Control	9.73(100)†	7.18(100)	10.67(100)	3.29(100)	2.00(100)
Gypsum	10.36(106)	9.08(126)	13.59(127)	7.16(218)	3.56(178)
Mixed & Limed	12.81(132)	11.13(155)	15.71(147)	7.92(241)	4.25(213)
$LSD_{0.05}$	2.18(22)	0.72(10)	1.24(12)	1.07(33)	0.58(29)

†Expressed as a percentage of the control.

The extent to which chemical amelioration of the profile by gypsum has taken place is illustrated in Table V. Although gypsum treatment had little effect on pH in either year, it did bring about substantial improvement in the Ca status of the profile while reducing the Al saturation. There was also a progressive improvement with time. Gypsum increased the total concentration of Al in the soil solution as a result of exchange but because of ion pair formation ($AlSO_4^+$) and the ionic strength effect, the activity of Al^{3+} was much reduced.

Table V. Effect of gypsum application on chemical properties of an Appling profile in 1984 and 1986 (Data of Sumner et al., 1986)

Depth	pH		Exchange complex saturation				Soil solution (1984)			
m	1984	1986	Al		Ca		Concentration		Activity	
			1984	1986	1984	1986	Al	Ca	Al^{3+}	Ca^{2+}
			%				M			
					Control					
0-0.15	6.20	5.97	0	2	87	85	0	1780	0.0	1120
0.15-0.30	4.99	5.22	51	40	34	38	13	420	4.2	344
0.30-0.45	4.74	4.99	58	42	28	33	12	400	3.8	174
0.45-0.60	4.74	4.77	66	53	23	25	11	250	4.0	114
0.60-0.75	4.90	4.69	76	60	12	19	10	160	4.0	72
0.75-0.90	4.85	4.69	80	71	14	14	9	70	3.0	37
0.90-1.05	4.92	4.71	85	74	9	12	10	40	4.0	28
					Gypsum					
0-0.15	6.73	6.94	0	2	94	85	0	7850	0.0	3630
0.15-0.30	4.90	5.25	28	27	61	57	15	4220	2.4	2537
0.30-0.45	4.89	5.03	35	16	55	66	15	2420	3.7	1486
0.45-0.60	4.88	4.99	43	34	47	49	14	1620	3.0	1123
0.60-0.75	4.74	4.94	52	34	38	48	13	980	3.0	741
0.75-0.90	4.78	4.76	64	42	29	27	12	750	3.3	606
0.90-1.05	4.80	4.75	65	53	29	32	10	480	3.2	408

This amelioration stimulated root proliferation in the gypsum treated subsoil as illustrated in Table VI. Gypsum treatment resulted in root penetration to greater depth in the subsoil and in addition roots on average were three times longer than in the control. Specific root length (root length per unit root mass) indicated that the roots in the gypsum treated soil *were* finer than in the control which would confer greater potential activity as far as water uptake was concerned. This is corroborated by the fact that over a 14 day period in 1984 roots in the gypsum treated profile extracted 50% more water down to a depth of 0.8 m than did-those in the control.

Table VI. **Effect of gypsum application on root distribution in an Appling profile (Data of Carter, 1986))**

Depth	**Root Mass**		**Root Length**		**Specific Root Length**	
m	**Control**	**Gypsum**	**Control**	**Gypsum**	**Control**	**Gypsum**
	$g\ m^{-3}$		**mm^{-3}**		**$m\ g^{-1}$**	
0-0.15	86.3	65.2	375.3	439.1	4.34	6.73
0.15-0.30	10.3	20.7	39.7	94.3	3.85	4.56
0.30-0.45	1.8	15.0	11.2	95.5	6.22	6.37
0.45-0.60	3.4	5.5	52.0	112.5	15.29	20.45
0.60-0.75	1.2	3.4	4.3	28.3	3.58	8.32
0.75-0.90	0.0	8.5	2.4	35.6	-	4.18
0.90-1.05	0.0	0.4	0.6	0.8	-	2.00
Total 0-1.05	102.9	118.7	484.7	806.2	-	-
Total 0.15-1.05	16.7	29.4	109.4	367.1	-	-

EXPERIMENT 3

The beneficial effect of gypsum on the production of maize grain is clearly illustrated in Table VII. In this experiment, significant yield responses to gypsum were obtained even in the first, year unlike the experiments in Georgia. In fact, yields on the gypsum treated plots were better in all years than those with deep lime incorporation because the depth of lime incorporation was probably less than in the Georgia experiments. The effect of gypsum on the Al and Ca saturation of the cation exchange capacity is essentially the same as was found in Georgia (Table VIII).

Table VII. Effect of gypsum and deep lime incorporation on yield of maize grain grown on a highly weathered acid soil in South Africa

Treatment	1983/84	Maize Grain 1984/85 metric tons ha^{-1}	1985/86
Control	4.77(100)†	7.78(100)	5.90(100)
Gypsum	5.81(121)	9.04(116)	7.05(119)
Deep Lime Incorp.	5.76(120)	8.48(109)	6.55(111)
$LSD_{0.05}$	0.53(11)	0.45(6)	0.37(6)

†Expressed as a percentage of the control.

Table VIII. Effect of gypsum application on exchangeable cation saturation and root density in a Normandien clay loam profile.

Depth	Exchange complex saturation Ca	 Mg %	 Al	Root density ML^{-1}
		Control		
0-0.15	48	44	3	3.1
0.15-0.30	38	40	15	2.9
0.30-0.45	14	14	61	1.8
0.45-0.60	11	15	62	0.5
0.60-0.75	8	16	74	0.1
0.75-0.90	9	16	74	0.0
		Gypsum		
0-0.15	70	23	3	3.0
0.15-0.30	66	25	6	1.6
0.30-0.45	50	27	19	2.0
0.45-0.60	35	25	36	3.9
0.60-0.75	13	19	64	2.0
0.75-0.90	11	18	67	1.7

The progressive movement of Ca down the profile with time and the consequent reduction of Al in the subsoil is well illustrated by these data. However Mg is also displaced downward by the gypsum as previously documented by Sumner et al. (1986). From a nutritional standpoint, this is a potential problem which is being investigated as one of the objectives of Experiment 4. From the data in Tables VII and VIII it is highly likely that the crop response to gypsum stems from better water utilization from deeper subsoil layer as roots penetrate deeper in much the same way as has been documented in the Georgia experiments.

EXPERIMENT 4

Thus far significant yield responses to gypsum application were only obtained in the first cut of alfalfa on this experiment but deep liming has resulted in a doubling of yield in 1986. The reason for the lack of response to gypsum probably lies in the deleterious effect it has had on the Mg level in this very sandy soil. The yield response to deep liming indicates that there is a subsoil rooting problem. Yield. responses to gypsum are visible in 1987 as a result of adequate topdressing of Mg to correct the acute imbalance induced by the gypsum. This imbalance is illustrated in Table IX. For topsoil, gypsum has caused a very marked decrease in exchangeable Mg which has become worse with time. This decrease in exchangeable Mg is probably the reason why only limited yield response to gypsum was observed in the first cropping season. Gypsum has also lead to a decrease in exchangeable K which may contribute to problems. A topdressing of KCl was made between samplings in 1985 and 1986 which explains the higher values in the latter. Gypsum decreased tissue K and Mg and increased Ca while a positive yield response to gypsum was only recorded at the lowest level added. Presumably the higher rates exacerbated the nutritional imbalance sufficiently to offset any benefit of the gypsum.

Table IX. Effect of varying rates of gypsum and deep liming on exchangeable cations in Tifton topsoil and on tissue composition and yield of the first cut of alfalfa in 1986

Treatment	Exchangeable						Tissue Composition			Yield
	Ca		Mg		K		K	Ca	Mg	
	1985	1986	1985	1986	1985	1986				
	cmmol(+)kg^{-1}						%			kg ha^{-1}
Control	1.18	1.19	0.25	0.30	0.12	0.25	2.55	0.94	0.22	868
2t Phospho-gypsum ha^{-1}	1.62	1.19	0.13	0.13	0.10	0.21	2.10	1.14	0.18	1096
5t Phospho-gypsum ha^{-1}	2.54	1.21	0.09	0.06	0.08	0.14	1.89	1.38	0.15	789
10t Phospho-gypsum ha^{-1}	3.79	3.12	0.15	0.06	0.10	0.14	1.96	1.41	0.14	746
Mixed & Limed	1.16	1.27	0.29	0.30	0.10	0.24	2.26	1.35	0.21	1669
LSD$_{0.05}$		0.49		0.04		0.03	0.20	0.14	0.02	186

POSSIBLE MECHANISMS FOR AMELIORATION

Before proceeding to enumerate the possible mechanism responsible for the ameliorative effect of gypsum on subsoils, it is pertinent to list the observed effects on subsoils which require explanation.

Gypsum

(a) reduces exchangeable Al and its activity in solution,

(b) increases exchangeable Ca and its solution activity,

(c) decreases exchangeable Mg and K

(d) causes little consistent change in pH with some evidence suggesting a slight increase with time.

It remains to develop and test hypothetical mechanisms which will account for the facts.

Ion pairing and complex formation

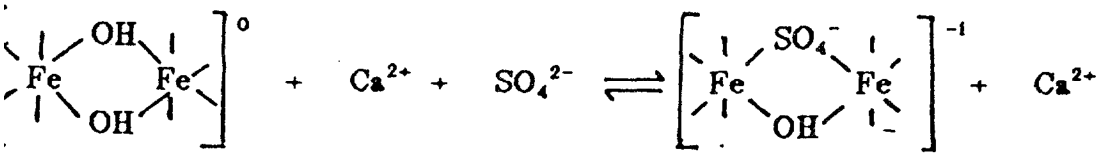
Pavan et al. (1982) were the first to suggest that the $AlSO_4^+$ ion pair readily formed in the presence of $CaSO_4$ was responsible for reducing the toxicity of Al in solution as follows:

$$Al^{3+} + Ca^{2+} + SO_4^{2-} \rightleftharpoons AlSO_4^+ + Ca^{2+}$$

They suggested that $AlSO_4^+$ is less toxic than Al^{3+}. The problem with verifying this hypothesis is the fact that one cannot obtain a solution consisting only of $AlSO_4^+$ ions as there is an equilibrium with Al^{3+} as indicated by the equation. In addition Al forms ion pairs and complexes with many ligands simultaneously in soil systems examples of which are $AlOH^{2+}$, $Al(OH)_2^+$, AlF_2^-, AlF_3^0, $AlPO_4^0$, etc. Furthermore it is difficult to separate out the effects of the individual ions in the detoxification process. Thus in the above equation, the presence of Ca^{2+} may stimulate root growth independent of the effect of SO_4^{2-} on Al^{3+}. In real soil systems, the situation is very complex and it is impossible to assign relative toxicities to the various ions, ion pairs and complexes which can be effectively and directly tested. Nevertheless the weight of evidence would suggest that these ion pairs and complexes are less toxic than A13+ (Alva et al., 1986a and b; Blarney et al., 1983; Pavan and Bingham, 1982).

"Self Liminq"

Reeve and Sumner (1972) proposed a mechanism whereby elevated levels of sulfate added to a soil would result in an exchange with solid phase OH groups resulting in the appearance of OH^- in solution which would complex with Al^{3+} as follows:



$$Al^{3+} + OH^- \rightleftharpoons AlOH^{2+}$$

Evidence for this increase in OH^- in solution has been presented by Sumner et al. (1986) and is summarized in Tables X and XI. Five years after gypsum application, soil pH in water is slightly higher down the entire profile on the gypsum treatment. Furthermore pH measured in 0.5 M K2S04 is consistently higher than in M KCl indicating that

Table X. Effect of gypsum on soil pH of an Appling profile five years after application

Depth m	Control			Gypsum		
		Soil pH in			Soil pH in	
	H_2O	M KCl	0.5 M K_2SO_4	H_2O	M KCl	0.5 M K_2SO_4
0-0.15	5.97	4.78	5.17	6.94	5.89	6.20
0.15-0.30	5.22	4.13	4.67	5.25	4.15	4.69
0.30-0.45	4.99	4.20	4.75	5.03	4.21	4.79
0.45-0.60	4.77	4.19	4.76	4.99	4.12	4.72
0.60-0.75	4.69	4.20	4.75	4.94	4.15	4.73
0.75-0.90	4.69	4.17	4.69	4.76	4.08	4.64
0.90-1.05	4.71	4.19	4.70	4.75	4.16	4.69

SO_4^{2-} does replace OH^-. Further corroboration is found in Table XI in which pH has been measured in $CaSO_4$ and $CaCl_2$ of the same molarity and ionic strength. Under all conditions, pH in CaSO4 is higher than the corresponding pH in $CaCl_2$ by about 0.1-0.3 pH units. The same effect has been demonstrated by Couto et al. (1979) and Singh (1982, 1984).

Table XI. Effect of nature and concentration of electrolyte on pH of Appling soil (Sumner et al., 1986)

Concentration or ionic strength mol L^{-1}	pH at given concentration in			pH at given ionic strength		
	$CaSO_4$	$CaCl_2$	pH	$CaSO_4$	$CaCl_2$	ΔpH†
0.0300	-	-	-	4.54	4.20	0.34
0.0140	4.42	4.14	0.28	4.72	4.44	0.28
0.0028	4.72	4.48	0.24	4.95	4.74	0.21
0.0014	4.82	4.62	0.20	5.08	4.91	0.17
0.0007	4.93	4.82	0.11	5.19	5.06	0.13

† $\Delta pH = pH_{CaSO4} - pH_{CaCl2}$

Mineral Precipitation

Good evidence is available (Adams and Rawajfih, 1977) to suggest the formation of compounds such as alunite ($KAl_3(OH)_6(SO_4)_2$) or basaluminite ($Al_4(OH)_{10}SO_4$) in acid soils as a result of elevated levels of SO_4^{2-} as illustrated in the reaction:

$$3Al^{3+} + K^+ + 2Ca^{2+} + 2SO_4^{2-} + 3H_2O \rightleftharpoons KAl_3(OH)_6(SO_4)_2 + 3H^+ + 2Ca^{2+}$$

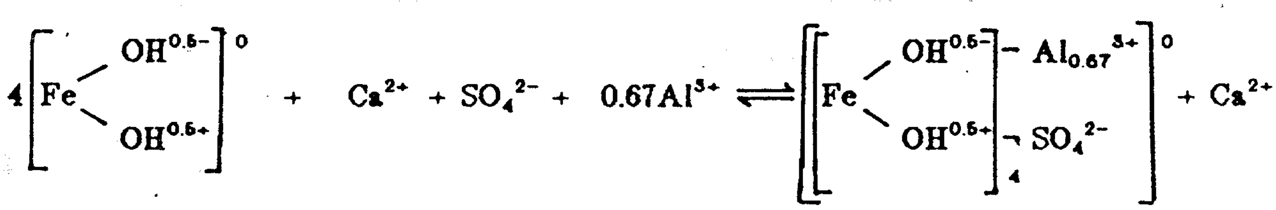
<u>Ionic Strength Induced Adsorption</u>

Some highly weathered soils exhibit ionic strength buffering (Fey et al., 1986) when a salt such as $CaSO_4$ is added whereas others do not. This behavior is illustrated by the data in Table XII by the differences in the composition of the soil solution after gypsum treatment. In the Appling topsoil, the soil solution reacted in a manner which would be predicted by exchange reactions (all ions and I increasing markedly) indicating that it exhibits little ionic strength buffering. In the subsoil completely different behavior is exhibited with Ca, SO_4 and I increasing but by amounts much less than in the topsoil and Al and K decreasing markedly. Over a number of highly weathered soils response to gypsum appeared to be linked to ionic strength buffering illustrated by the following reaction:

Table XII. Effect of gypsum on soil solution composition of two soils with different ionic strength buffering.

Soil	Treatment	Soil Solution Composition					
		Al	Ca	Mg	K	SO_4	I
		mmol L^{-1}					
Appling topsoil	None	0.008	1.68	0.55	0.33	0.13	7.8
	2t gypsum ha^{-1}	0.071	8.47	1.06	0.36	6.95	29.8
Appling subsoil	None	0.005	0.02	0.01	0.10	0.12	1.1
	2t gypsum ha^{-1}	0.003	0.83	0.22	0.04	1.12	5.4

I = ionic strength



CONCLUSIONS

1. Phosphogypsum reduces exchangeable and solution Al.
2. Phosphogypsum increases exchangeable and solution Ca.

3. Amelioration effected above allows roots to penetrate subsoil.
4. Increased root density in subsoil allows extraction of water previously unavailable to the crop.
5. Improved water availability leads to increased yields.
6. The effect seems to be long lasting in excess of 5 years after initial single application

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REFERENCES

Adams, F. and Z. Rawajfih. 1977. Basaluminite and alunite: A possible cause of sulfate retention by acid soils. Soil Science Society of America Proceedings 41:686-692.

Alva, A. K., D. G. Edwards, C. J. Asher, and F. P. C. Blarney. 1986a. Effects of phosphorus/aluminum molar ratio and calcium concentration on plant response to aluminum toxicity. Soil Science Society of America Journal 50:133-137.

Alva, A. K., D. G. Edwards, C. J. Ahser, and F. P. C. Blarney. 1986b. Relationships between root length of soybean and calculated activities of aluminum monomers in nutrient solution. Soil Science Society of America Journal 50:959-962.

Blarney, F. P. C., D. G. Edwards, and C. J. Asher. 1983. Effects of aluminium, OH:Al and P:Al molar ratios, and ionic strength on soybean root elongation in solution culture. Soil Science 136:197-207.

Carter, E. A. 1986. Improved alfalfa yield by modification of an acid subsoil. 16th National Alfalfa Symposium Proceedings, Purdue University pp. 97-108.

Couto, W., D. J. Lathwell, and D. R. Bouldin. 1979. Sulfate sorption by two Oxisols and an Alfisol of the tropics. Soil Sci. 127:108-116.

Fey, M. V., A. D. Noble and M. E. Sumner. 1986. Gypsum induced K fixation in highly weathered acid soils. Agronomy Abstracts 78:167.

Hammel, J., M. E. Sumner, and H. Shahandeh. 1985. Effect of physical and chemical profile modification on soybean and corn production. Soil Science Society of America Journal 49:1508-1512.

Pavan, M. A., and F. T. Bingham. 1982. Toxicity of aluminum to coffee seedlings grown in nutrient solution. Soil Science Society of America Journal 46:993-997.

Reeve, N. G., and M. E. Sumner. 1972. Amelioration of subsoil acidity in Natal Oxisols by leaching surface applied amendments. Agrochemophysica 4:1-6.

Singh, S. S. 1982. Effect of chloride and sulfate anions on the chemical characteristics of some acid soils. Canadian Journal of Soil Science 62:549-557.

Singh, S. S. 1984. Increase in neutral salt extractable cation exchange capacity of some soils as affected by $CaSO_4$ applications. Canadian Journal of Soil Science 64:153-161.

Sumner, M. E. 1970. Aluminum toxicity - a growth limiting factor in some Natal sands. Proceedings South African Sugar Technology Association 44:197-203.

Sumner, M. E., W. P. Miller, D. E. Radcliffe and M. McCray. 1986. Use of phosphogypsum as an amendment for highly weathered soils. Proceedings Third Phosphogypsum Symposium, Florida Institute of Phosphate Research, Bartow, Florida.

Sumner, M. E., H. Shahandeh, J. Bouton and J. Hammel. 1986. Amelioration of an acid soil profile through deep liming and surface application of gypsum. Soil Science Society of America Journal 50:1254-1258.

THE EFFECT OF SOIL AMENDMENT WITH PHOSPHOGYPSUM ON CLAY DISPERSION, SOIL CONSERVATION, AND ENVIRONMENTAL QUALITY

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ABSTRACT

Highly weathered soils of the southeastern U.S. generally have poor physical properties, low infiltration rates, and high erodibilities, due in part to the easily dipersible nature of the soil clays. This dispersion, caused by low electrolyte concentrations in the soils, results in crusting and sealing of the soil under rainfall, with loss of water to runoff and high soil loss rates. The use of gypsum, particularly highly soluble phosphogypsum, is shown to increase infiltration rates and reduce soil loss of these soils by flocculating the clay, preventing it from. sealing the soil surface and contributing to soil erosion. Gypsum is able to maintain sufficiently high ionic strengths in solution to overcome the dispersive nature of these clays, resulting in less clay content of sediments and less potential for sediment contamination of surface waters. While the longevity of this effect in the field is not known, current estimates suggest that improved yields and decreased erosion will justify the use of phosphogypsum in many agronomic situations, and perhaps in other sediment control applications in urban areas.

INTRODUCTION

Traditionally the major soil factors considered to limit plant growth have been related to the nutrient-supplying capacity of soils, or soil fertility and chemistry. However, a greater awareness is emerging that soil physical properties may have significant impacts on plant growth, particularly in the southeastern U.S., where soils are highly weathered with generally poor physical condition. There is increasing interest in the causes and effects of deteriorated soil tilth, partially due to the economic pressures to increase productivity and on-farm efficiency. Environmental concerns also are demanding reduced soil degredation in the interest of long-term soil productivity, and maintanence of surface water quality that is threatened by agricultural sediment generated from poorly managed soils.

The soil physical properties of most relevance to the above problems are degree and stability of aggregation and the related factors of macro-porosity, infiltration rate, and soil erodibility. Aggregation is the phenomenon of primary soil particles (sand, silt, and clay) interacting to form larger agglomerates, resulting in the creation of large macro-pores that are the major water-conducting pores. Without stable aggregates, permeability is slowed, rainfall runs off and generates erosion, and water that should have been stored in the soil for plant use instead carries sediments to contaminate surface waters. Of primary importance in formation of these aggregates is the behavior of the finest particles in the soil, the clay: it may act as a cement to bind aggregates together (along with soil organic matter, or humus), or it may "disperse" and allow the disintegration of aggregates and subsequent blockage of water-conducting pores.

FLOCCULATION/DISPERSION PROCESSES

In colloid chemistry, the study of the behavior of clays and other very small (< 2u) particles, **dispersion** is defined as the formation of a stable suspension of particles in water, caused by the mutual repulsion of these particles due to the presence of extensive negative electric fields generated by the particles themselves. Dispersion is enhanced by factors increasing the magnitude and extent of this field: presence of large monovalent cations (Na^+) around the particle surfaces; increased pH, which generates more charge by deprotonating hydroxyls on the clay surfaces; and low electrolyte concentration in solution, providing few cations to counter-balance the negative charge and "compress" the thickness of the electric field. **Flocculation** is the opposite process, whereby the electric field (or double layer) is sufficiently compressed so that attractive van der Waals forces allow coagulation into micro-aggregates to occur (van Olphen, 1977).

In field soils, flocculation is a necessary condition for the formation and cementation of larger aggregates that will encourage water inflow and resist erosion. This is most apparent in sodic soils found in semi-arid regions, where insufficient leaching has allowed Na to remain in the soil. Dispersion in these soils results in poor aggregate formation or stability, few macro-pores, and very slow permeability associated with severe crusting of the soil surface (Shainberg and Lety, 1984). Management is extremely difficult due to water ponding, low subsoil water availability, and poor seedling emergence through the hard surface crust.

Well-leached temperate region soils are better flocculated due to the presence of Ca^{+2} cations that compress the double layers and allow particles to coagulate. However, the clays in these soils will disperse with aggitation, as with shaking in water or under the impact of raindrops at the soil surface (Emerson, 1967). Early soil conservation studies suggested that dispersion in such soils may promote increased soil erosion (Middleton, 1930), and more recently low-Na soils in Australia and Israel have been shown to be dispersive, largely due to low electrolyte contents caused by extensive weathering (Shainberg et al., 1981: Rengasamy et al., 1984). Thus it appears that either insufficient leaching in very "young" soils, leaving dispersive Na in the soil, or excessive leaching in very "old" soils, where few cations remain to aid flocculation, can result in dispersion related problems.

USE OF GYPSUM ON DISPERSIVE SOILS

Gypsum has been successfully used on sodic soils for a number of years to improve soil flocculation and aggregation and thereby increase water infiltration and reduce crusting (Rinehart et al., 1953; Loveday, 1984). High loadings of gypsum tend to cause replacement of dispersive Na^+ with Ca^{+2} on clay surfaces, and subsequent leaching away of the Na. The results in the field are increased macro-porosity and much improved infiltration rates, making the soils more productive and easier to manage (Agassi et al., 1982; Chartres et al., 1985).

Some highly weathered, non-sodic soils also respond favorably to gypsum applications, where the increased solution electrolyte concentration causes clay flocculation and an almost instantaneous improvement in infiltration (Loveday, 1974; Shainberg et al., 1982). Under simulated rainfall soils from Israel and South Africa have shown significant improvements in infiltration with gypsum application, as dispersion is reduced via the ionic strength effect (Agassi et al., 1985; du Plessis and Shainberg, 1985).

Keren et al. (1981) have demonstrated the benefits of phosphogypsum in ameliorating dispersive soils. It is more soluble, and more rapidly soluble, than mined sources of gypsum, particularly when a fine particle size is used. For low-Na soils where surface crusting is a problem, surface application without incorporation is the preferred application method, as more soluble gypsum is present at the point of raindrop impact where prevention of dispersion is most critical.

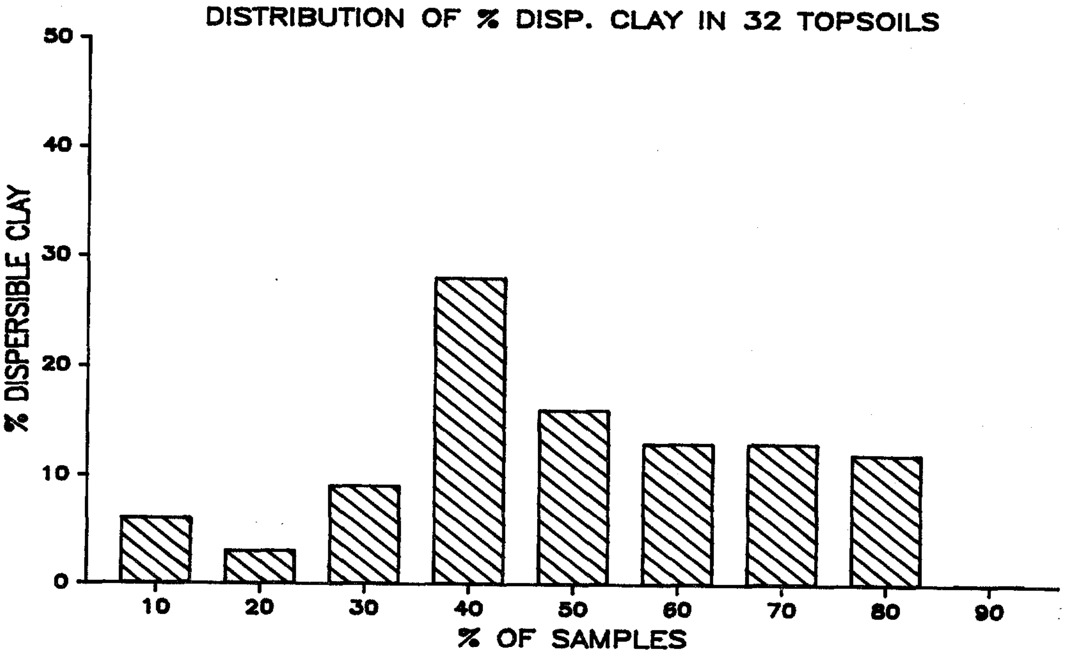
DISPERSION IN SOUTHEASTERN SOILS

Early studies by Middleton (1930) and Peele et al. (1947) suggested that highly weathered Ultisols of the southeast were dispersive, and that this characteristic was involved in the low infiltration rates and high soil loss observed on these soils. While dispersion is not widely accepted as a degredative process in the more intensively studied Midwestern soils, current findings identify it as a major factor enhancing runoff and erosion in the Southeast.

EROSION AND INFILTRATION

The results of a study assessing the dispersibility of a range of Southeastern soils is presented in Figure 1. Dispersibility here is defined as the percentage of the total clay fraction (determined using chemical dispersants) that is dispered in water after 12 hr of shaking on an end-o,ver-end shaker (Miller and Miller, 1987). The modal value of 40%, with a skewed distribution toward higher values, indicates the relative ease of dispersion of these soils. The

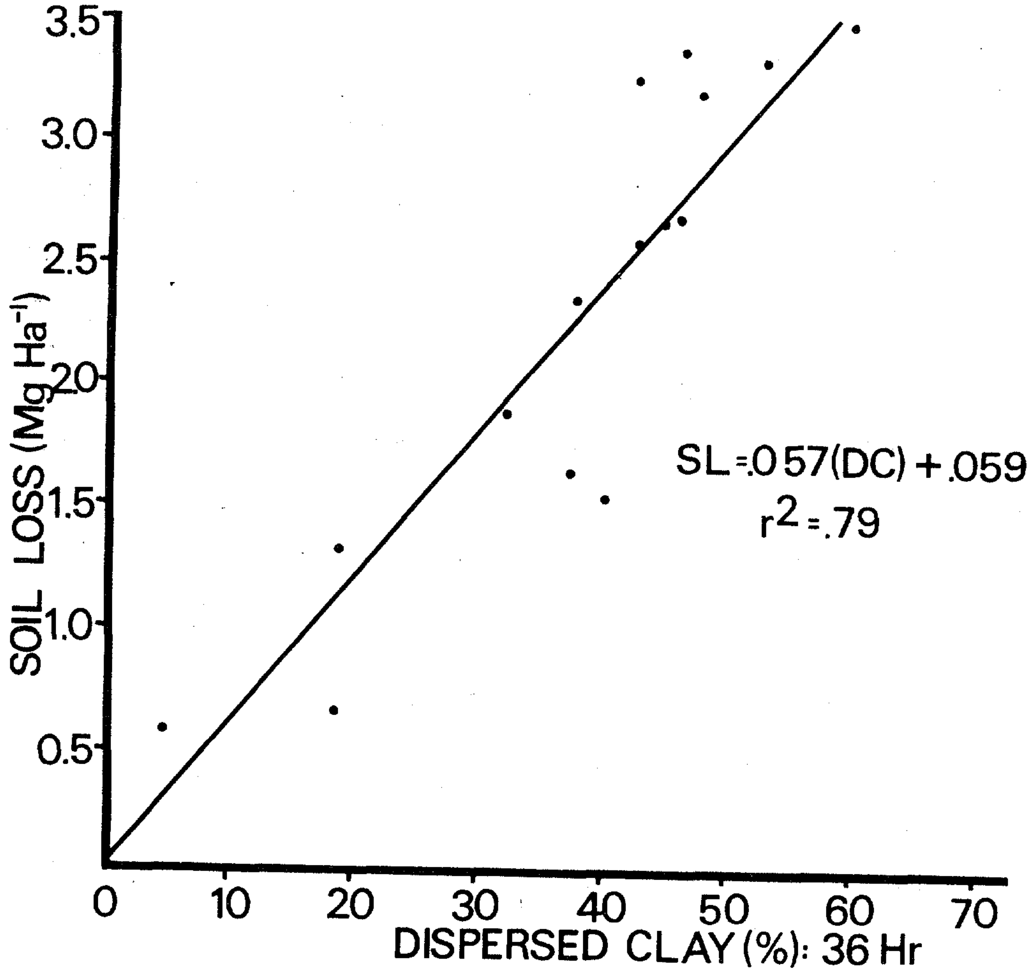
Figure 1. Dispersibility of selected southeastern topsoils.



clay that is dispersed is likely to form "washed-in" layers of low permeability under raindrop impact, which is simulated by the shaking of the soil/water mixture in the lab test (Agassi et al., 1985).

In a study of 15 Georgia topsoils, clay dispersion, aggregation, and a number of other soil parameters were related to infiltration and soil loss measured in small pan studies under a rainfall simulator (Miller and Baharrudin, 1986; 1987). Soils packed in 0.36x0.20 m pans on a 9% slope were exposed to 20 min of 11.2 cm/hr rainfall, with collected runoff and sediment used to calculate infiltration and soil loss. Clay dispersion was measured by shaking soil in water at a 8:1 water:soil ratio over various time intervals. A significant inverse relationship was found between % dispersible clay and infiltration rate (r = -0.59*), indicating that the presence of increasing amount of dispersed clay was involved in pore sealing and lowered infiltration. The pro-

Figure 2. Regression of dispersion *vs.* soil loss for 15 Georgia topsoils.



portion of clay dispersed after 36 hr of shaking was also an excellent predictor of total soil loss from the pans (Figure 2). This relationship reflects both the actual contribution of dispersed clay to the total sediment lost from the pans, and the added effect of pore sealing that promotes more runoff and further loss of coarser soil particles. No other soil property studied was as highly correlated with infiltration and soil loss as clay dispersion, although several aggregation parameters were negatively related to soil loss (Miller and Baharrudin, 1987).

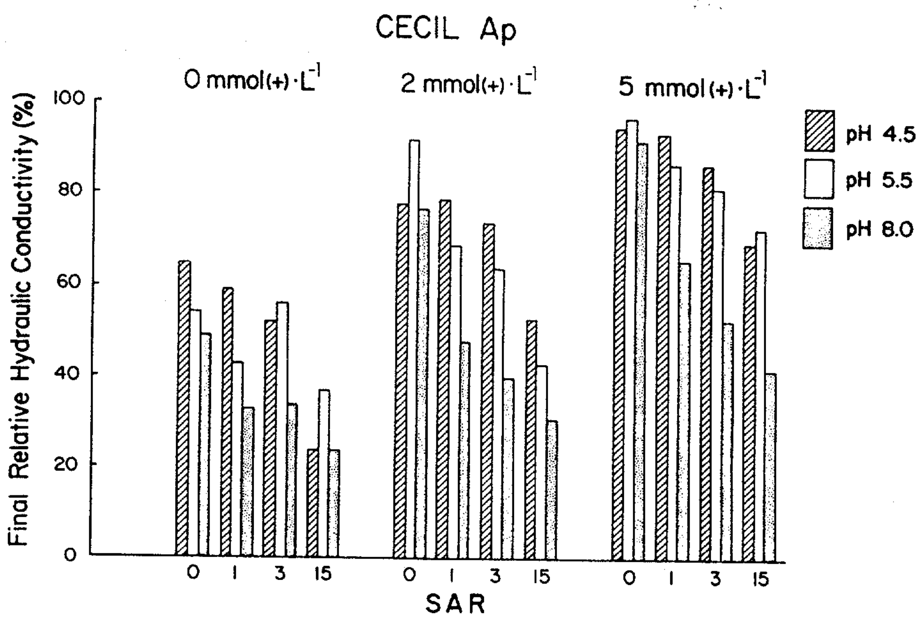
PERMEABILITY AND DISPERSION

The effect of dispersive cations and low electrolyte concentrations on soil permeability (hydraulic conductivity) has been known for some time (Quirk and Schofield, 1955). However, traditional appraisals of the amounts of exchangeable Na causing dispersion and reduced permeability have been challenged, as McIntyre (1979) has shown serious declines in conductivity with as little as 5% Na on soil colloid surfaces.

In a study of 3 Southeastern Ultisols, Chiang et al. (1987) examined the effect of soil pH, Na percentage, and electrolyte concentration on hydraulic conductivity. Soil columns were initially leached with concentrated mixed Na/Ca solution of varying sodium adsorption ratios (SAR) in order to adjust percentages of exchangeable Na to various levels. Then dilute solutions of the same SAR were applied to the columns, and the rate of water flow relative to that of the concentrated solutions determined. These tests were repeated with soils adjusted to different pH levels.

The results for the Cecil topsoil (Figure 3) show that the permeability of this material was affected by all three variables examined, but most dramatically by electrolyte concentration. Conductivities at 0 mmol/L (deionized water) were reduced to less than 60% of the values obtained in the concentrated salt solutions, with even Ca-saturated soil (SAR = 0) showing relatively low permeability. Increasing

Figure 3. **Effect of solution parameters on hydraulic conductivity of Cecil soil.**

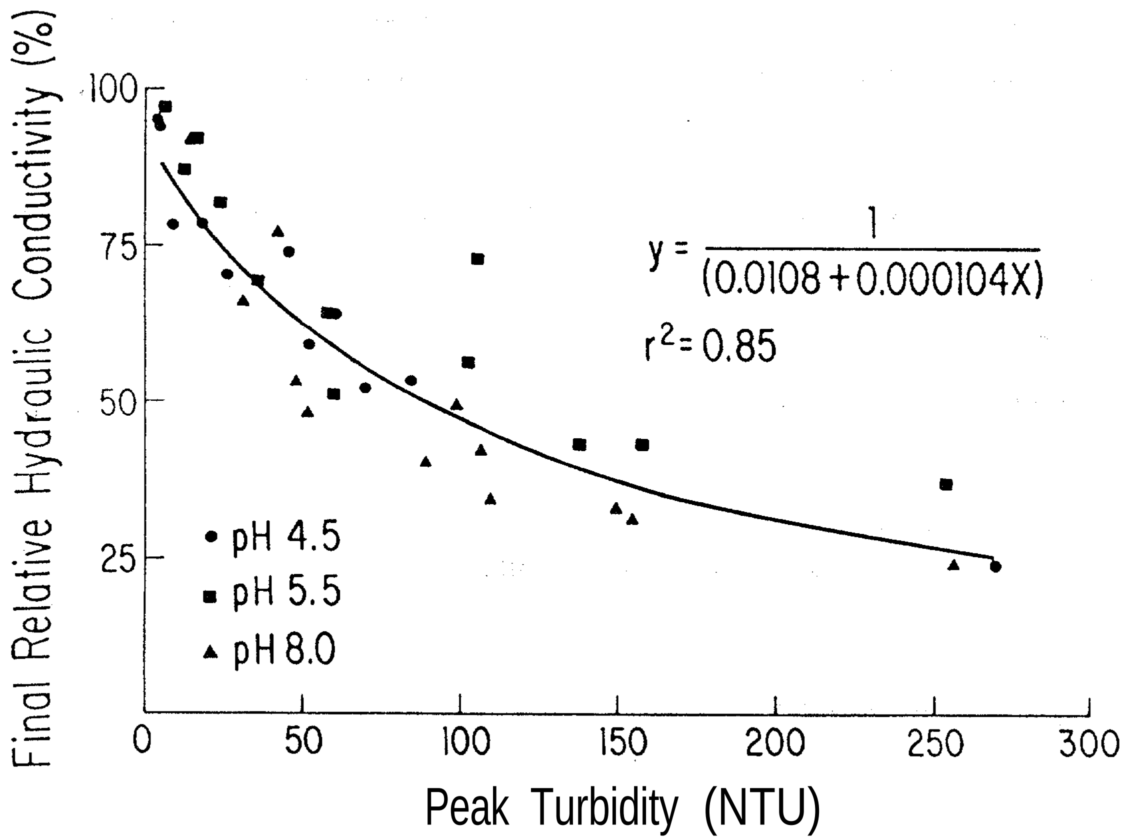


pH and Na levels resulted in progressive declines in conductivity. Solutions of 2 mmol/L and 5 mmol/L increased water flow rates, but as little as 1-3 % Na (equivalent to SAR = 1-3) caused declines in conductivity. The other soils studied showed similar trends, although they were not as sensitive to the lower Na levels.

Other studies of Na-induced declines in conductivity have identified swelling of smectitic minerals as the major mechanism involved, and have not found significant reductions in permeability with non-swelling kaolinitic soils (McNeal and Coleman, 1966). As Frenkel et al. (1978) suggested, clay dispersion is the factor involved in the conductivity declines observed in Southeastern soils. For the three soils studies by Chiang et al. (1987), the significant relationship between turbidity of the leachate (a measure of dispersed clay) and relative conductivity demonstrates that permeability declines as greater amounts of dispersed clay block water transmission pores (Figure 4).

The data from these studies show that clay dispersion is a major factor regulating infiltration, hydraulic conductivity, and soil erosion on highly weathered Southeastern soils. The combined deleterious effects of low Na levels, low electrolyte concentrations, and high pH are responsible for this dispersion. Management of these soils must take dipersive processes into account in order to optimize pro-

Figure 4. Relationship of leachate turbidity to hydraulic conductivity of Cecil soil.



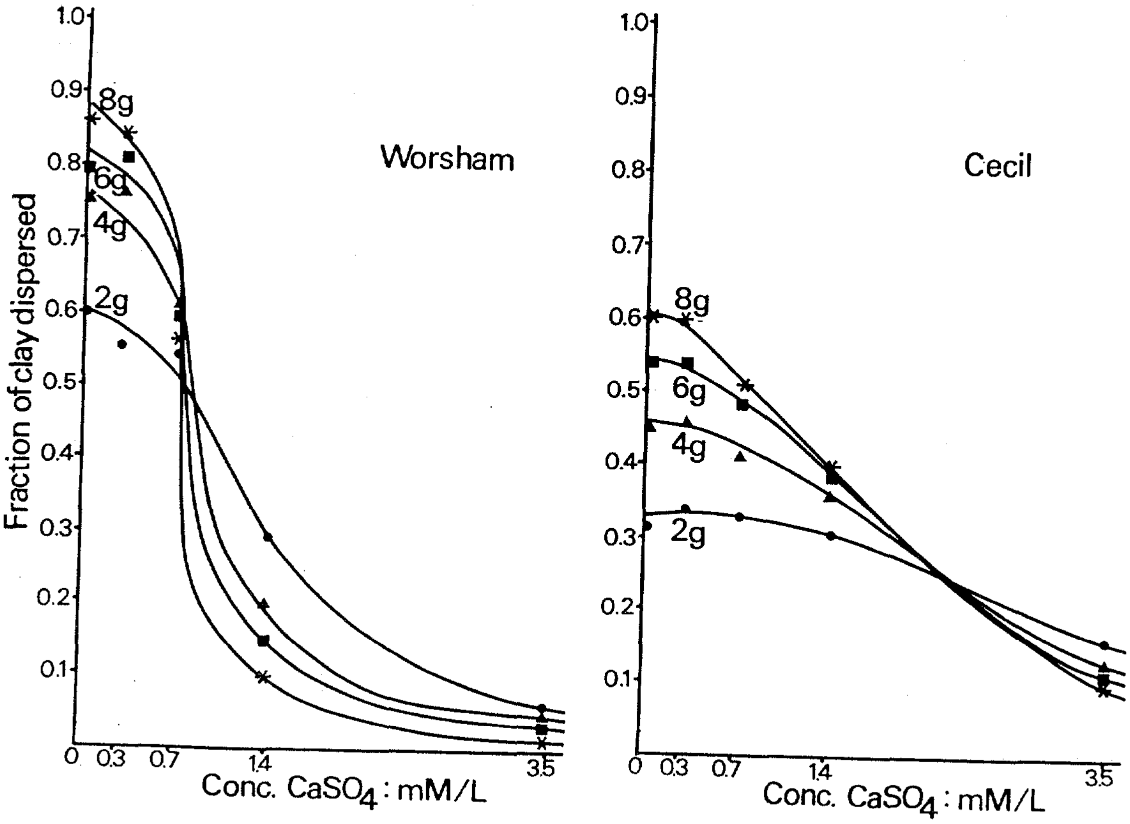
duction and safeguard environmental quality. Current studies indicate the use of gypsum may play a significant role in reaching these objectives.

EFFECT OF GYPSUM ON DISPERSION

The dual effects of increased electrolyte concentration and Ca^{+2} replacement of Na^{+} suggest that gypsum may prove effective in flocculating clays in highly weathered soils, and thereby improve their physical properties and water relations significantly.

In a laboratory study of several Georgia soils, various weights of dried, < 2 mm soil were mixed with 40 mL of a range of $CaSO_4$ solutions in order to determine the concentration at which flocculation occurred after 24 hr shaking. For the Cecil topsoil, the fraction of the total soil clay dispersed in pure H_2O increased with decreasing soil weight, suggesting that increasing dilution with water increased the dispersibility of the soil clays (Figure 5). Increasing

Figure 5. Dispersion of two soils as affected by soil weight and $CaSO_4$ concentration.

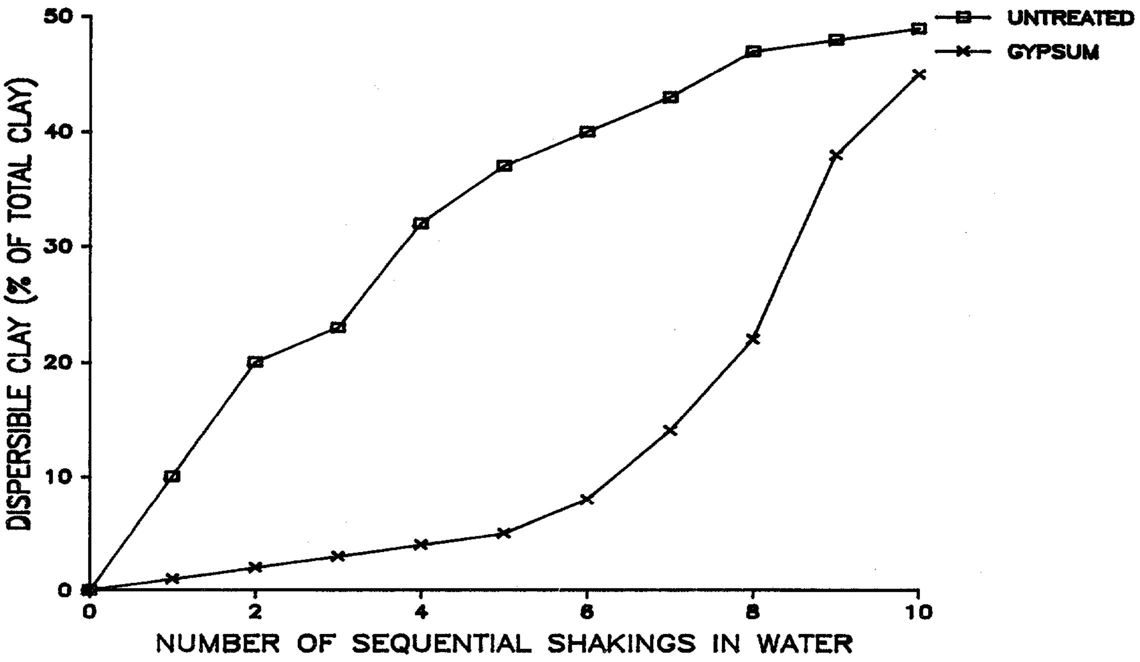


concentrations of gypsum resulted in flocculation of the clays, with dispersion reaching a minimum at 2-3.5 mmol/L. The Worsham soil was much more highly dispersive at low concentrations, but flocculated rapidly at all soil weights with about 1 mmol/L $CaSO_4$. Similar studies on other soils show that dispersion is prevalent below 1-3 mmol/L, with fairly sharp decreases in dispersion above those concentrations. Given that typical soil solution Ca^{+2} concentrations in Georgia soils are in this same range of 1-3 mmol/L, it is apparent that in the field, soil clays are balanced on the edge between flocculation and dispersion. with the impact of raindrops on bare soil to catalyze dispersion and the addition of high-purity rainwater to dilute soil solutions at the soil surface, it is not surprising that deflocculation occurs.

The promise of gypsum in promoting flocculation is that it is soluble up to 15 mmol/L, which is more than adequate to inhibit dispersion. Of the various gypsum sources, phosphogypsum has a finer particle size, higher purity, and more rapid solubility than most mined gypsum. Within a few minutes it dissolves to form solutions greater than 5-7 mmol /L, and is thus ideal for surface applications to soil where rapid dissolution under rainfall conditions is critical to maintaining high electrolyte concentrations.

Clay dispersibility of field plot samples amended with phosphogypsum is shown in Figure 6, compared with untreated control plots. The soil is a Cecil series that had recieved 5 mt/ha phosphogypsum 1 year previous to sampling. Four g samples were shaken 15 min with 40 ml deionized water, dispersed clay measured by pipette (Miller and Miller, 1987), and fresh deionized water added after centrifugation and decantation. The method simulated the dilution that occurs under rainfall conditions in the field. The gypsum-treated samples remained flocculated until the sixth cycle of dilution, at which time the electrolyte concentration had de-

Figure 6. Dispersion of untreated and phosphogypsum-treated field soils with sequential shaking in water.



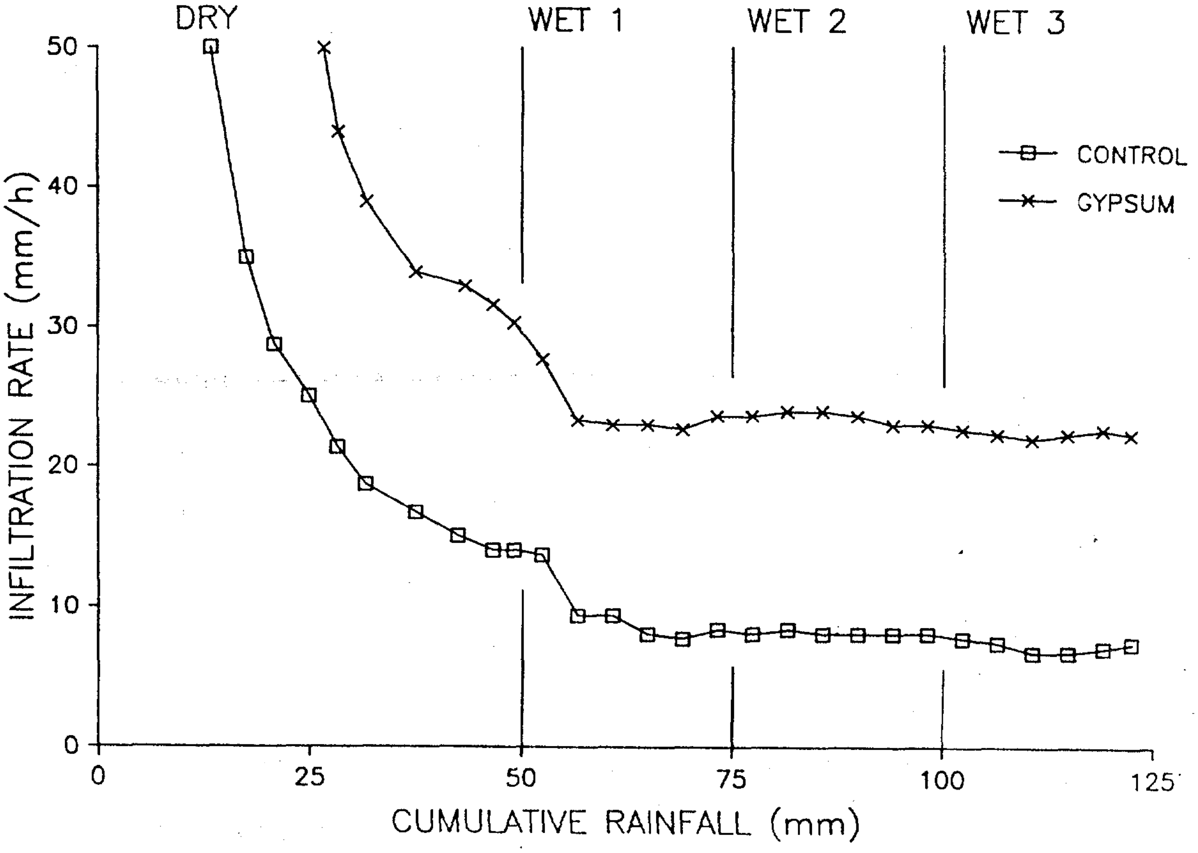
clined to < 1 mmol/L (data not shown), and dispersion occurred. The longevity of the gypsum effect in the field will likely depend on this ability to maintain an ionic strength sufficiently high to exceed the flocculation concentration of the soil clays.

INFILTRATION AND SOIL LOSS STUDIES

As discussed previously, laboratory studies have shown that applications of gypsum to field soils will prevent seal formation and maintain higher infiltration rates of low-Na soils (Agassi et al., 1982; du Plessis and Shainberg, 1985). A series of experiments, described in detail by Miller (1987), was designed to demonstrate this effect on highly weathered Southeastern soils, using phosphogypsum as the gypsum source. Three upland sandy loam topsoils from the Georgia Piedmont were packed into 0.3 m^2 runoff pans, and either amended with 5 mt/ha equivalent of 60-mesh phosphogypsum or left untreated. Simulated rainfall, was applied at 5 cm/hr for 1 hr, followed 24 hr later by 3 successive 0.5 hr events at the same intensity. Runoff was collected over time and used to determine sediment lost land and infiltration rates of the soils.

Infiltration rate of the Cecil soil over approximately 125 mm of applied rainfall is shown in Figure 7, for the phosphogypsum treated and untreated control soils. The

Figure 7. Infiltration rates of Cecil soil under simulated rainfall as affected by phosphogypsum treatment.



values shown are means of three replicate determinations, and infiltration rates at each time show a significant treatment effect at the 5% probability level. By the end of the first hour of rainfall (the "dry" event), the untreated soil was badly crusted, with infiltration rate declining to less than 12 mm/hr, while the gypsum-treated soil was still near 30 mm/hr. Over the three subsequent "wet" events, the infiltration rate of the control soil stabilized at 8-9 mm/hr, while the gypsum-amended soil maintained a rate of nearly 25 mm/hr. Average infiltration values for the three soils are presented in Table 1, showing that the Wedowee soil gave results similar to the Cecil, while the Worsham, a severely crusting soil in the field, showed less significant gypsum effect during the later wet events.

Also shown in Table 1 are soil loss values for the three soils as affected by gypsum amendment. The untreated Cecil soil showed a relatively low erodibility, and the gypsum treatment decreased soil loss only during the dry event, probably due largely to the delay in runoff time and the greater infiltration rate (Figure 7). Soil loss on the other two soils was significantly reduced over each rainfall event on the phosphogyspum-amended soils.

Table 1. Infiltration and soil loss for three untreated and gypsum-amended soils under simulated rainfall.

	CECIL		WORSHAM		WEDOWEE	
	Control	Gypsum	Control	Gypsum	Control	Gypsum
Cumul. infil.(mm)						
:Dry event	29.7	43.3	11.8	20.4	12.5	30.7
:All events	43.9	79.6	15.8	27.9	18.1	48.7
Final infil. rate (mm/hr)	8.5	23.6	1.6	3.1	3.6	10.7
Total soil loss (kg/ha)	727	501	3762	1922	2846	1322

The implications of these findings are potentially important to both short- and long-term crop growth. As water availability will be significantly increased in gypsum-amended soils due to higher infiltration under rainfall, some part of the yield response to gypsum reported by Hammel et al. (1986) may be a direct result of lesser sealing due to improved flocculation with gypsum treatment. In the long term, less soil erosion will maintain productivity of these soils.

ENVIRONMENTAL ASPECTS OF GYPSUM USE

Besides enhancing soil productivity, gypsum use may play an important role in protecting water quality. Sediment and associated agricultural chemicals are a major water pollutant in many surface waters. The colloid fraction of the soil, if in a dispersed condition, is particularly liable to contaminate water, not only causing increased water turbidity but also releasing adsorbed nutrients and pesticides to chemically contaminate drinking water and wildlife habitat (Alberts et al., 1980).

The capacity of gypsum to flocculate clay has been discussed previously, and is further evident in examination of sediment particle size data obtained from the infiltration studies described above. Percent clay in the sediments of the three soils studied is shown in Table 2, where it is evident that phosphogypsum has the capacity to nearly completely flocculate any clay-sized particles generated in the sediment of these soils. The untreated soils have considerable sediment clay contents, indicative of the easily dispersed nature of the clay fractions of these soils. In the Southeast this clay is a major water pollutant, as evidenced by common high turbidity levels in stream and river waters (Trimble, 1974). Gypsum promotes flocculation of clay-sized particles into larger silt-sized aggregates (data not shown) which are less transportable than the finer clay. On a field scale this should result in greater effectiveness of conservation measures such as grass strips and terraces in retaining sediments, and less subsequent transport to surface waters.

Table 2. Clay content and electrical conductivities of sediments from three gypsum-amended and untreated soils.

	CECIL		WORSHAM		WEDOWEE	
	Control	Gypsum	Control	Gypsum	Control	Gypsum
% clay in sediment						
:Dry event	15	3	23	3	30	0
:All events	13	1	23	2	31	2
Elec. conductivity						
:Ave-Dry event	0.06	1.02	0.05	1.33	0.05	1.27
:Ave-All events	0.01	0.51	0.02	1.28	0.02	1.08

The flocculating action of gypsum should find other applications in water clarification and sediment control. Its use in sediment control basins, on construction sites, and along roadways may aid in controlling sediment delivery from disturbed urban lands, and also aid in revegetation of these areas. The high solubility and purity of phosphogypsum, and its low cost, suggest it as an ideal material for these applications. Some concerns regarding trace contaminants such as cadmium and radionuclides in by-product gypsum should be addresses before wide-spread use of the material; however, the low content of these contaminants in most by-product material will likely not pose a threat to the environment (Mays and Mortvedt, 1986).

CONCLUSIONS

Aggregation of soil is a major contributing factor to its behavior in the field with regard to rainfall acceptance, surface crusting, and soil erosion. Flocculation of the clay fraction is a particularly crucial component of aggregation in highly weathered soils, as dispersion of the clay under raindrop impact has the potential to crust these soils in a manner analogous to the same process in sodic soils. Gypsum applications to these soils increase the electrolyte concentration to a level sufficient to insure flocculation of the clay fraction. In runoff pan studies this flocculating effect results in greater infiltration and lesser soil loss levels than untreated soils. This should promote both short-term increases in soil productivity due to increased water availability, and maintain long-term productivity by reducing soil degredation via erosion. In addition, gypsum use on agricultural soils sharply reduces the clay content of sediments, thereby protecting adjacent surface waters from this highly mobile pollutant source.

The major questions to be resolved in implimenting gypsum use in agriculture in the Southeast center on application rates, timing, and economics. The longevity of the gypsum effect on field soils has not been established; current data suggest only that 5 mt/ha maintains infiltration over 12-15 cm of rainfall, or perhaps 2 months in the field. Longer term field experiments are underway to assess infiltration over an entire growing season. The cost/benefit analysis of gypsum use will have to be determined using yield data in conjuction with benefit assessment associated with environmental concerns. The use of by-product phosphogypsum from Florida sources should reduce costs to users; given the yield gains reported in the Piedmont of Georgia (see Sumner et al., this proceedings), the economics of gypsum use on many crops should be favorable. The relatively low cost of phosphogypsum recommends its use in urban sediment control as well, should further experimentation demonstrate its potential in sediment control in this area as well.

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REFERENCES CITED

Agassi, M., J. Morin, and I. Shainberg. 1982. Laboratory studies of infiltration and runoff control in semi-arid soils in Israel. Geoderma 28:345-356.

Agassi, M., J. Morin, and I. Shainberg. 1985. Effect of raindrop impact energy and water salinity on infiltration rates of sodic soils. Soil Sci. Soc. Am. J. 49:186-190.

Alberts, E. E., W. C. Moldenhauer, and G. R. Foster. 1980. Soil aggregates and primary particles transported in rill and interrill flow. Soil Sci. Soc. Am. J. 44:590--595.

Chartres, C. J., R. S. Greene, G. W. Ford, and P. Rengasamy. 1985. Effects of gypsum on macro-porosity and crusting of two red duplex soils. Aust. J. Soil Res. 23:467-479.

Chiang, S. C., D. E. Radcliffe, W. P. Miller, and K. D. Newman. 1987. Hydraulic conductivity of three southeastern soils as affected by sodium, electrolyte concentration, and pH. Soil Sci. Soc. Am. J. 51:(In Press).

du Plessis, H. M., and I. Shainberg. 1985. Effect of exchangeable sodium and phosphogypsum on the hydraulic properties of several South African soils. S. Afr. J. Plant Soil 2:179-185.

Emerson, W. W. 1967. A classification of soil aggregates based on their coherance in water. Aust. J. Soil Res. 5: 47-57.

Frenkel, H., J. O. Goertzen, and J. D. Rhoades. 1978. Effects of clay type and content, exchangeable sodium percentage, and electrolyte concentration on clay dispersion and soil hydraulic conductivity. Soil Sci. Soc. Am. J. 42: 32-39.

Hannel, J. E., M. E. Sumner, and H. Shahandeh. 1985. Effect of physical and chemical profile modification on soybean and corn production. Soil Sci. Soc. Am. J. 49:1508-1511.

Keren, R., and I. Shainberg. 1981. Effect of dissolution rate on the efficiency of industrial and mined gypsum in improving infiltration of a sodic soil. Soil Sci. Soc. Am. J. 45:103-107.

Loveday, J. 1974. Recognition of gypsum-responsive soils. Aust. J. Soil Res. 25:87-96.

Loveday, J. 1984. Amendments for reclaiming sodic soils. p. 220-237. In I. Shainberg and J. Shalhevet (Eds.) Soil salinity under irrigation. Springer-Verlag, New York.

Mays, D. A., and J. J. Mortvedt. 1986. Crop response to soil applications of phosphogypsum. J. Environ. Qual.15:78-81.

McIntyre, D. S. 1979. Exchangeable sodium, subplasticity, and hydraulic conductivity of some Austrialian soils. Aust. J. Soil Res. 17:115-120.

McNeal, B. L., and N. T. Coleman. 1966. Effect of solution composition on soil hydraulic conductivity. Soil Sci. SOC. Am. Proc. 30:308-312.

Middleton, H. E. 1930. Properties of soils which influence soil erosion. U.S.D.A. Tech. Bull. No. 178. 16 p.

Miller, W. P. 1987, Infiltration and soil loss -of three gypsum-amended Ultisols under simulated rainfall. Soil Sci. Soc. Am. J. 51:(In Press).

Miller, W. P., and M. K. Baharrudin. 1986. Relationship of soil dispersibility to infiltration and erosion of southeastern soils. Soil Sci. 142:235-240.

Miller, W. P., and M. K. Baharrudin. 1987. Interrill erodibility of highly weathered soils. Commm. Soil Sci. Plant Anal. 18:(In Press).

Miller, W. P., and D. M. Miller. 1987. A micro-pipette method for soil mechanical analysis. Comm. Soil Sci. Plant Anal. 18:1-5.

Peele, T. C., E. E. Lathan, and O. W. Beale. 1945. Relation of the physical properties of different soil types to erodibility. S. Carol. Ag. Exp. Stn. Bull. No 357.

Quirk, J. P. 1978. Some physico-chemical aspects of soil structural stability-A review. p. 3-16. In W. W. Emerson, R. D. Bond, and A. R. Dexter (Eds.) Modification of soil structure. Wiley and Sons, New York.

Quirk, J. P., and R. K. Schofield. 1955. The effect of electrolyte concentration on soil permeability. J. Soil Sci. 6:163-178.

Rengasamy, P., R. S. B. Greene, G. W. Ford, and A. H. Mehanni. 1984. Identification of dispersive behavior in the management of red-brown earths. Aust. J. Soil Res. 22:413-422.

Rinehart, J. C., G. R. Blake, J. C. F. Tedrow, and F. E. Bear. 1953. Gypsum for improving the drainage of wet spots. New Jersey Ag. Expt. Sta. Bull. NO. 772. 15 p.

Shainberg, I., R. Keren, and H. Frenkel. 1982. Response of sodic soils to gypsum and calcium chloride applications. Soil Sci. Soc. Am. J. 46:113-117.

Shainberg, I., and J. Lety. 1984. Response of soils to sodic and saline conditions. Hilgardia 52(2):1-57.

Shainberg, I., J. D. Rhoades, D. L. Suarez, and R. J. Prather. 1981. Effect of mineral weathering on clay dispersion and hydraulic conductivity of sodic soils. Soil Sci. Soc. Am. J. 45:287-291.

Trimble, S. W. 1974. Man-induced soil erosion on the Southern Piedmont, 1700-1970. Soil Cons. Soc. Am., Ankeny, IA.

van Olphen, H. 1977. An introduction to clay colloid chemistry. Second ed. Wiley and Sons, New York.

EFFECTS OF PHOSPHOGYPSUM AND LIME ON YIELD, ROOT DENSITY, AND FRUIT AND FOLIAR COMPOSITION OF APPLE IN BRAZILIAN ACID SOILS.

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ABSTRACT

Field experiments were conducted with two acid soils in the State of Paraná, Brazil, to evaluate the effects of soil applications of phosphogypsum and calcitic lime on the chemistry of the soil profile and resultant response of apple trees (*Malus domestica* Borkh. cv. Gala/MM 106). One orchard was on a low Ca, and high Al; the second orchard was on a low Ca and low Al. Lime was more efficient than phosphogypsum in reducing Al_{ex} and increasing Ca_{ex} in the surface horizon. Subsoil pH, Al_{ex} and Ca_{ex} were not affected by surface applied lime; however, phosphogypsum decreased Al_{ex} and increase Ca_{ex} throughout the soil profile. There was a close relationship between Ca^{2+} and Al^{3+} in soil solution and root growth, leaf-and fruit-Ca, and apple (fruit) yield. Lime increased root growth in the surface horizon (0-20 cm) only, but phosphogypsum increased root growth to the depth of 60 cm at the site containing Al_{ex}. This increase in root lenght is ascribed to $CaSO_4^o$ leaching into the subsoil and thus increasing the availability of Ca in the subsoil as well as SO_4 reducing the concentration of Al_{ex} in the subsoil. Significant increases in fruit production ocurred during the 1986 harvest at both sites for the lime and phosphogypsum treatments. However, fruit production was greater for the phosphogypsum treatment at the site containing Al_{ex}. Soil application of lime and phosphogypsum appears to be an important management tool in addition to foliar sprays and post harvest dips for influencing the Ca status of apple fruit.

INTRODUCTION

Apple (*Malus domestica* Borkh.) has been one of the principal commercial fruit crops in the State of Parana, Southern Brazil. Apple orchards are established on soils which are highly weathered and contain kaolinite, gibbsite, and iron oxides and hydroxides as the dominant clay minerals (Pavan, et al., 1985) - These soils contain low cation exchange capacity (CEC) and concentrations of Ca, Mg, and K and relatively high exchangeable Al. These Fe-Al-rich oxisols develop positive charged sites which strongly adsorb phosphate and sulfate. As a consequence of these chemical and mineralogical characteristics, root penetration into the subsoil is limited. Thus, apple yields are marginal unless the soil has been properly limed and fertilized.

Under this soil condictions, one would expect responses to Ca-applied salts since the Ca ion is know to be involved in many fundamental physiological plant processes. Post harvest physiology disorders such as bitter pit in apples have been linked to low Ca content of the fruit (van der Boon, et al., 1970). However, apple responses to Ca-salts applied to the surface of soils are variable. Therefore, we established a study in 1984 to investigate the effects of soil applications of calcitic lime ($CaCO_3$) and phosphogypsum on soil chemistry and Ca nutrition of apple.

MATERIALS AND METHODS

Two orchards containing six year old apple tree (Malus domestica Borkh.) were chosen in each of two important apple growing soils in the southern part of the State of Parana, Brazil. The trees were 'Gala' cultivar grafted on MM 106 rootstock. The soils at both sites are acid and low in exchangeable bases. Exchangeable Al was only present at Site I (see Table I for general chemical properties).

The experimental treatments were: (i) control (no Ca source); (ii) $CaCO_3$ to elevate the soil pH to 6.0; and (iii) phosphogypsum (30% CaO, 17% SO_4, and 0.2% P_2O_5) added in equivalent amount to the $CaCO_3$ rate. The fertilizer management consists of applying 100, 65, and

TABLE I

Soil characteristics for the two apple orchards sampled prior to application of treatments. The soil data pertain to the 0-20 cm horizon.

Site	pH	Exchangeable cations $(\mathrm{Cmol(p+)kg^{-1}})$					Org. Carb.	P
	0.01m $CaCl_2$	Al	Ca	Mg	K	Total acidity	(%)	$(\mathrm{mg\ kg^{-1}})$
I	4.7	1.4	0.3	0.2	0.5	9.6	1.6	6
II	5.0	0.0	0.4	0.2	0.3	4.5	0.7	18

83 kg ha^{-1} y^{-1} of the N, P, and K, respectively, as urea, triple superphosphate and KCl.

The three treatment were replicated three times in a completely randomized block design. Each treatment consisted of 15 trees in 3 rows with 5 trees per row. Rows were spaced 4 m apart with 1.5 m between trees within each row. Only the center three trees of the middle row were used for sampling. The trials were initiated April 1984.

Soil samples were taken annually in July from each plot near the edge of the tree canopy for the following depths: 0-10, 10-20, 20-40, 40-60, 60-80, and 80-l00 cm. The following procedures were used to analyze the soil samples. Soil pH was measured in 0.01 M $CaCl_2$ (soil solution ratio of 1:2.5), Ca, Mg, and Al were extracted by M KCl and K and P by the double acid (0.05 M HCl + 0.025 H_2SO_4). These extractions were carried out with a soil:solution ratio of 1:10 with a shaking time of 10 min. Ca and Mg were determined by atomic absorption spectrophotometry (AAS); Al by the colorimetric method using ferron; K by flame photometry; and P by phosphomolybdate blue colorimetric method. Saturation extracts from those samples were prepared and analyzed (Rhoades, 1982) .

In the week of January 15, 1385 and 1986 leaf samples were taken, using the fourth leaf from the base of annual shoots for chemical analysis. In all, thirty leaves per replicate were collected. The leaves were washed with deionized water, oven-dried at 65°C for 48 hours, ground, and then digested with concentrated HNO_3 and HCl prior to Ca analysis by AAS.

At harvest, twenty randomly selected fruits per each replicate were used for Ca analysis. Fruits were washed with deionized water, peeled, sliced, and air-dried for 3 days following oven-drying at 65°C for 48 hours. The dried samples were then ground, and digested in a mixture of concentrated HNO_3 and HCl acids. The digests were analyzed for Ca by AAS.

The root sampling procedure consisted of digging one hole on each side 1 m from the trunk of the three trees under observation per replicate. Generally, root sampling was located near the outer edge of the foliage canopy. Soil samples were taken to a depth of 1 m, in 10 cm intervals, in January 1986. The barrel type auger used to obtain the samples was 7 cm diam. x 10 cm high. All roots were washed from the soil cores, cleamed and the root length was measured by the procedure described by Tennant (1975).

RESULTS AND DISCUSSION

SOIL DATA

The effects of treaments on pH and exchangeable Ca, Mg, and Al, two years after applications, are shown in Table II. Lime significantly increased pH in the top-surface (0-10 cm), indicating that little movement of lime occurred below the 10 cm depth. Phosphogypsum had two distinct effects on soil reaction: (i) Site I pH decreased in the 0-60 cm layer, and there was no change in pH of soil profile below 60 cm depth; and (ii) Site II - pH increased slightly in the top-surface (0-10 cm) only. The decrease in pH of Site I after application of phosphogypsum, was probably due to salt-induced hydrolysis of Al-hydroxide minerals with subsequent release of H^+ ions (Thomas and Hargrove, 1984). The resulting acidity can be neutralized by OH^- release by ligand exchange with dissolved SO_4^{2-}, Because of its high Al content, H^+ release exceeded OH^- release in the Site I, causing pH to decrease. In the low Al site (Site II), OH^- release dominated, with resulting pH increase.

The application of $CaCO_3$ and phosphogypsum resulted in significantly increased levels of exchangeable Ca (Ca_{ex}). Lime was more efficient than phosphogypsum in increasing Ca_{ex} in the top-layer (0-10 cm) because of the marked effect of pH on the pH dependent CEC of those soils (Pavan, et al., 1985) as well as an abundant supply of Ca. However, $CaCO_3$ had no effect on Ca_{ex} in the subsoil. Phosphogypsum application substantially increased the Ca_{ex} level in Site-I in the 0-40 cm layer. Concomitant with increase Ca_{ex}, the levels of Mg_{ex} and Al_{ex} decreased with depth to 60 cm. The increase in Ca_{ex} in the subsoil of Site I was due to displacement of Al_{ex} and Mg_{ex} and possibly

TABLE II

Effects of amendments on soil chemical characteristics.

Soil Depth	Site I			Site II		
	Control	Lime	Phosphogypsum	Control	Lime	Phosphogypsum
	pH (0.01 M $CaCl_2$)					
0 - 10	4.8	6.7	4.6	4.9	6.5	5.2
10 - 20	4.6	5.0	4.4	4.9	5.2	5.1
20 - 40	4.6	4.6	4.4	4.7	4.8	4.7
40 - 60	4.6	4.6	4.5	4.7	4.7	4.8
60 - 80	4.5	4.5	4.5	4.7	4.7	4.6
80 - 100	4.5	4.5	4.5	4.7	4.6	4.7
	Al (Cmol $(p+)kg^{-1}$)					
0 - 10	1.22	---	0.68	---	---	---
10 - 20	1.60	0.82	0.52	---	---	---
20 - 40	1.42	1.10	0.60	---	---	---
40 - 60	1.02	1.00	0.72	---	---	---
60 - 80	1.00	1.00	0.81	---	---	---
80 - 100	1.00	1.10	1.00	---	---	---
	Ca (Cmol $(p+)kg^{-1}$)					
0 - 10	0.92	7.0	2.26	0.36	3.62	1.92
10 - 20	0.76	4.26	2.00	0.30	1.90	0.80
20 - 40	0.30	0.58	1.80	0.22	0.64	0.40
40 - 60	0.26	0.30	1.00	0.20	0.30	0.32
60 - 80	0.26	0.30	0.82	0.10	0.18	0.16
80 - 100	0.30	0.30	0.40	0.10	0.10	0.10
	Mg (Cmol $(p+)kg^{-1}$)					
0 - 10	0.40	0.34	0.26	0.28	0.20	0.16
10 - 20	0.26	0.30	0.20	0.20	0.16	0.18
20 - 40	0.16	0.16	0.12	0.20	0.18	0.22
40 - 60	0.18	0.18	0.16	0.22	0.20	0.18
60 - 80	0.08	0.10	0.10	0.18	0.20	0.16
80 - 100	0.08	0.08	0.10	0.20	0.20	0.16

--- undetectable

due to some Ca occupying variable charge sites that were created by the increase ionic strength of the soil solution following the phosphogypsum application. Phosphogypsum reduced Al_{ex} due to either the formation of Al-hydroxy-sulfate mineral at low pH (Sposito, 1985) or by sulfate-induced Al polymerization following ligand exchange for hydroxyl groups (Reeve and Sumner, 1972).

The saturation extract data sampled at the second year of the experiment were chemically speciated using the GEOCHEM speciation model (Sposito and Mattigod, 1980). Lime increased the concentration of $Ca^{2}+$ and decreased Al^{3+} in the 0-10 cm layer. Phosphogypsum resulted in SO_4^{2-} ion-pairing with Al and Ca to form AlSOi and $CaSO_4^0$, thereby decreasing the concentration of Al^{3+} and Ca^{2+} in soil solution, Therefore, for Site I, although phosphogypsum decreased pH, there were at least two benefits: (i) decreased concentration of Al^{3+}, and (ii) increased Ca_{ex} in the 0-60 cm layer due to leaching of Ca as uncharged specie ($CaSO_4^0$) and consequentely displacement of Al_{ex} and Mg_{ex} .

PLANT DATA

The influence of the treatments on root length and distribution in the soil profile is shown in Table III. As expected there is a close relationship between root length and the concentration of Ca and Al in the soil profile. Because of the accumulation of Ca in the 0-20 cm, horizon, $CaCO_3$ increased the root growth in the top surface (0-20 cm) only. Phosphogypsum produced two interesting effects: (i) Site I, phosphogypsum increased root growth to the depth of 60 cm, probably due to decreased Al^{3+} and increased Ca^{2+} in soil solution; and (ii) Site II, the phosphogypsum application did not affect significantly root growth, due to the leaching of Ca as $CaSO_4^0$ rather than as Ca^{2+}, the latter being more available.

According to the leaf analysis for 1986, treatments with lime and phosphogypsum significantly increase leaf Ca at both sites. (Table IV). The addition of phosphogypsum to Site I caused an increase in the Ca content of the foliage and fruit (Table IV); however, at Site II only the leaf Ca increased. Such results imply direct tree response to soil moisture and deeper root distribution. The deeper root growth

TABLE III

Influence of amendments on the root density of soil horizon sampled January 1986

Soil	Root Density (cm g^{-1})			LSD
Depth	Control	Lime	Phosphogypsum	P = 0.05
		Site I		
0 - 10	52	132	118	18
10 - 20	60	68	108	10
20 - 60	16	18	89	9
		Site II		
0 - 10	80	144	110	13
10 - 20	108	110	100	11
20 - 60	32	36	44	8

induced by the phosphogypsum treatment promoted an increase in water and Ca uptake. In general, this result suggests that the uptake of Ca by apple roots was influenced not only by the Ca species in solution (Ca^{2+} > $CaSO_4^0$) but also the rate of movement of the ion to absorbing roots.

In 1986, only the phosphogypsum treatment resulted in leaf Ca values exceeding 1.5% Ca (Table IV), which is considered the lower level of the normal range for leaf Ca in a survey of fruit tree nutrition (Shear and Faust, 1980).

In 1986 for Site I the yields of apples were higher in phosphogypsum treatment. Such result may be explained in terms of increasing deeper root growth under phosphogypsum treatment at Site I. However for Site II, the yield per tree was higher in lime treatment due to increase the availability of Ca in the top-surface of limed plots.

CONCLUSIONS

Soil applications of lime or phosphogypsum in two apple orchards planted on acidic and low Ca soils resulted in greater apple root development, larger fruit, and enhanced vailability of Ca to both leaves and fruit. Phosphogypsum was more effective than lime to reduce subsoil acidity and to improve deeper root growth in soil containing exchangeable Al. Lime or phosphogypsum appear to be important management tools for influencing the Ca status of apple fruit in acid brazilian soils.

REFERENCES

Chapman, H. D. 1964, Suggested foliar sampling and handling techniques for determining the nutrient status of some field horticultural and plantation crops, Indian J. Hort. 21:97-119.

Pavan, M. A.; F. T. Bingham, and P.F. Pratt. 1985. Chemical and mineralogical characteristics of selected acid soils of the State of Parana, Brazil. Turrialba 9:131-139.

TABLE IV

Influence of amendment on leaf-and fruit-Ca
concentration and apple yield in 1986

Treatment	Leaf-Ca	Fruit-Ca	Yield
	----- %(dry wt basis)	--------	kg/tree
	Site I		
Control	1.04	0.029	4.4
Lime	1.42	0.029	6.6
Phosphogypsum	1.58	0.035	9.1
LSD (P=0.05)	0.36	0.003	2.0
	Site II		
Control	1.18	0.029	4.2
Lime	1.42	0.035	8.2
Phosphogypsum	1.40	0.029	6.9
LSD (P=0.05)	0.29	0.003	2.2

Reeve, N.G. and M.E. Sumner. 1972. Amelioration of subsoil acidity in Natal oxisols by leaching surface applied amendments. Agrochmophysica, 4:1-6.

Rhoades,J.R, 1982. Soluble salts. In A.L. Page (ed.) Methods of soil analysis. pt. 2. Chemical and microbiological properties. Agronomy 9 (3nd ed.): 167-179.

Shear, C.B. 1975. Calcium nutrition and quality in fruit crops. Commun. Soil Sci. Pl. Anal. 6:233-244.

Sposito, G. 1985. Chemical model of weathering in soils. In J. I. Driver (ed.) The chemistry of weathering. D. Reidel Publishing Company, New York. p. 1-18.

Sposito, G. and S.V. Mattigod. 1980. GEOCHEM. A computer program for the calculation of chemical equilibria in soil solutions and other natural water systems. Kearney Foundation of Soil Sci., Univ. of California, Riverside. 110p.

Tennant, D. 1975. A test of a modified lime intersect method of estimating root length. J. Ecol. 63:995-1001.

Thomas, G.W. and W.L. Hargrove. 1984. The chemistry of soil acidity. In F. Adams (ed.) Soil acidity and liming. Am. Soc. Agron., Madison, Agronomy 12: 3-56.

Van der Boon, J.; B. J. van Goor, and L.K. Wiensum. 1970. Discussion meeting on bitter pit in apple. Tech. Commun. Int. Soc. Hort. Sci. Haren-Groninger 15-16. 4. 1969. Acta Hort. no. 16.

CALCINATION

STUDIES ON THE LIME SENSITIVITY OF PHOSPHOGYPSUM

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ABSTRACT

Lime sensitivity is referred to in the literature and the plaster industry as the unpredictable physical properties of phosphogypsum which is usually neutralised with lime prior to conversion to calcined gypsum (calcium sulfate hemihydrate, plaster of Paris, plaster, stucco) and plaster products. These properties are: a very long setting time, a high water requirement of the slurry, and a decrease in the mechanical strength of cast specimens due to incomplete hydration of calcined phosphogypsum.

This paper explores the cause and remedy of lime sensitivity and gives recommendations on how to avoid it during the manufacture of plaster products from phosphogypsum.

INTRODUCTION

Phosphogypsum resulting from the manufacture of phosphoric acid by wet processes contains a number of impurities, mainly PO_4^{3-}, F^-, plexes of Fe^{3+} and Al^{3+}, organic matter, etc., which influence the setting properties of calcined gypsum (plaster or stucco) made from it. The most common and most harmful impurity is believed to be residual orthophosphoric acid, making the material acidic.

In industry phosphogypsum is usually neutralised with lime before conversion to calcined gypsum and plaster products. However, it is known that the material which has been neutralised with lime has a long setting time or will not set at all, resulting in poor or no strength in the cast specimens. In the literature (Wirsching, 1978) and industry this is referred to as lime sensitivity, caused by the formation of secondary calcium orthophosphate dihydrate, $CaHPO_4.2H_2O$, in situ (Berry, 1972; Beretka, 1982) during neutralisation.

This paper discusses the cause of lime sensitivity using the results of studies on 'model' systems containing 0.1 to 0.5% P_2O_5 and CaO. The findings are verified from data on three industrial phosphogypsums containing increasing levels (0.09, 9.38, and 0.73% respectively) of soluble P_2O_5.

EXPERIMENTAL

(a) The model system (Beretka, 1982; Beretka and Brown, 1983) consisted of calcined natural gypsum to which known amounts of both orthophosphoric acid (expressed as P_2O_5) and CaO were added.

The kinetics of hydration were estimated from the increase in temperature of the slurry when it set (exotherm), and the data were processed according to the Ridge equation (Ridge, 1964; Ridge et *al.*, 1972). The values of velocity constant (k), which is a measure of self-acceleration of the hydration, and (α_0), the measure of the extent of heterogeneous necleation in the system, i.e. the effective fraction of the dihydrate present at the beginning of the hydration, were calculated. The period of induction (θ), a parameter closely related to setting time, and defined as the time taken for the rate of increase in temperature to exceed 0.2°C, was also obtained from the exotherms. The physical properties of plaster slurries, viz. setting time, water requirement, and pH, and of cast gypsums, viz. mechanical strength, density, combined water content, and mineralogical composition, were determined by conventional methods (Beretka and Brown, 1983).

(b) The three industrial phosphogypsums (Beretka and Brown, 1986) containing 0.09, 0.38, and 0.73% of soluble P_2O_5, respectively, were calcined to the 'second boil' as in industry and then neutralised with CaO. For convenience, the lime addition, i.e. the degree of neutralisation, was expressed in terms of the CaO/P_2O_5 weight ratio, ranging from 0 to 5.

RESULTS AND DISCUSSION

Figure 1 shows the changes in kinetic parameters (Beretka, 1982) of calcined natural gypsum to which a fixed amount, 0.2%, of P_2O_5 and increasing amounts of CaO were added. The velocity constant, k, which is a measure of self-acceleration of the hydration, increases slightly up to a CaO/P_2O_5 weight ratio of 0.5, decreases to a minimum at about 1.0, and then increases again towards a stable value as the CaO/P_2O_5 ratio is increased further. The measure of the extent of heterogeneous nucleation in the system, α_0, is extremely low for weight ratios below 0.5, increases some 20-fold between the weight ratios of 1 and 2, and increases more moderately at higher weight ratios.

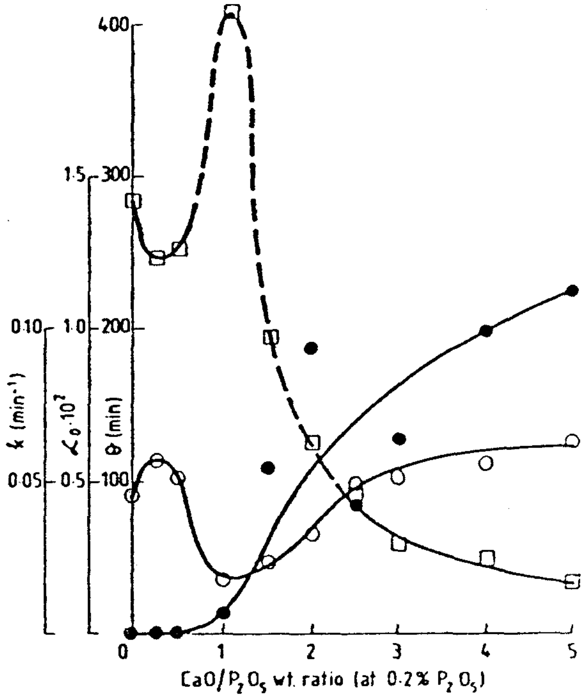

Figure 1. Changes in the kinetic parameters of the model system: ○ - the velocity constant k; ● - the measure of heterogeneous nucleation α_0: □ - the period of induction θ.

Variation in the period of induction, θ, a parameter closely related to setting time, agrees well with those of the other two parameters. In particular, small additions of CaO up to a weight ratio of 0.5 has relatively little effect on the induction period. However, at weight ratios above 0.5, θ increases rapidly, reaching a maximum of over 400 min at about 1 to 1.5, then decreases rapidly to more acceptable values for weight ratios of 2.5 to 3, after which it becomes constant. The results indicate that if orthophosphates are formed in situ they act as extremely strong retarders of the hydration of hemihydrate.

Figure 2 shows the changes in physical properties (Beretka and Brown, 1983) of the plaster slurries and cast specimens of calcined natural gypsums to which a fixed amount of 0.3% P_2O_5 was added, together with increasing amounts of CaO to give CaO/P_2O_5 weight ratios over the range from 0 to 5.

The setting time (curve (a)) increases rapidly to about 600 min at a weight ratio of about 1 to 1.5. It decreases rapidly to more practical values of 25 to 30 min as the CaO/P_2O_5 weight ratio increases.

The water requirement (b) shows a slight decrease at a weight ratio of about 0.5 to 0.75, after which it gradually increases over the range studied.

The pH (c) of the slurry increases with increasing weight ratio, as expected, showing the greatest increase in the weight ratio range of 1-2.

The compressive strength (d) of the cast specimens reaches a minimum of 3.6 MPa at a weight ratio of about 1.5. Above the weight ratio of about 2, the values of compressive strength increase and become similar to values usually reported for commercial cast gypsums.

The combined water contents (e) of air-dried specimens show a marked decrease from a nominal 19 to 20% to 14.8% at a weight ratio of about 1.5. This indicates that less water is required (and retained) in the specimens due to incomplete hydration of the hemihydrate in the weight ratio range of 1 to 2.

Finally, XRD (f) indicated that, at the weight ratio range of 1-2, the hydrated and set specimens contained up to 43% unreacted hemihydrate. Above the weight ratio of 2, virtually complete hydration has occurred, and very little or no hemihydrate can be detected in the cast specimens.

Figure 3 shows the effect of the addition of CaO on the physical properties of one industrial phosphogypsum (Beretka and Brown, 1986) containing 0.38% soluble P_2O_5. Here, there was a marked increase in setting time (a) from 6 to 30 min, a gradual increase in water requirement (b), an expected increase in pH (c), a sharp drop in compressive strength (d) from about 11 to 2 MPa, a large decrease in combined water content (e) from about 17 to 12%, and up to 58% unreacted hemihydrate (f) in the system, within the CaO/P_2O_5 weight ratio range of 1 to 2. In fact, the above changes in physical properties occurred at the same CaO/P_2O_5 weight ratio range, and were of about the same magnitude, as in the model system containing 0.3% P_2O_5 shown in Figure 2.

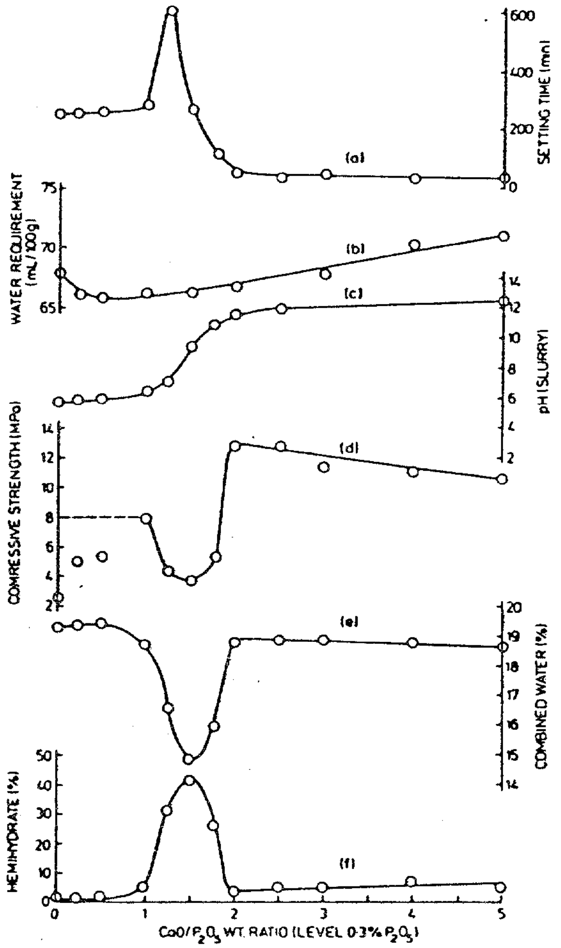

Figure 2. Changes in the physical properties of the model system containing 0.3% P_2O_5.

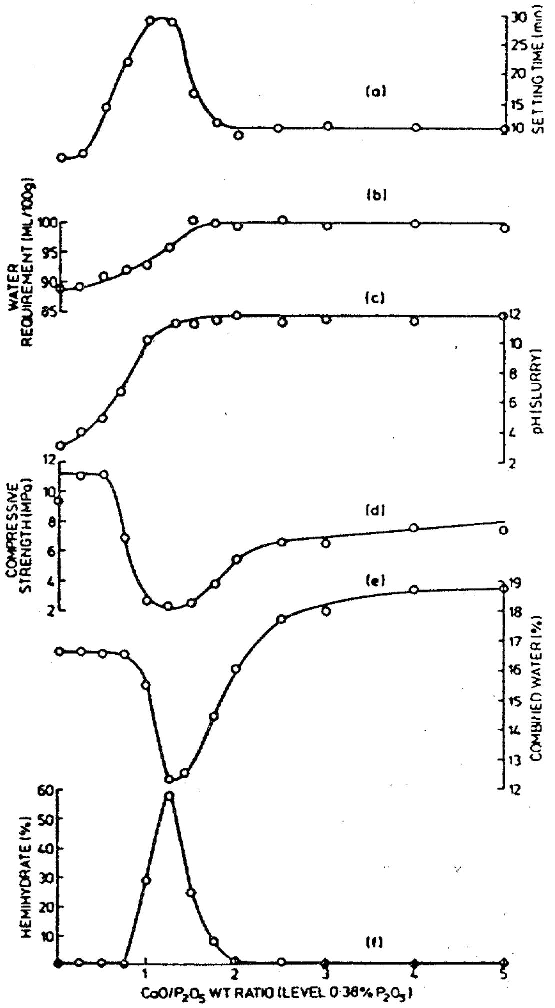

Figure 3. Changes in the physical properties of industrial phosphogypsum containing 0.38% P_2O_5.

CONCLUSIONS

Lime sensitivity of calcined phosphogypsum is due to the formation of secondary orthophosphates *in situ,* which act as powerful retarders in the plaster-water system. Very small concentrations, e.g. 0.1 to 0.3% P_2O_5 of the materials greatly affect the physical properties of cast specimens in the CaO/P_2O_5 weight ratio range of 1 to 2. Therefore, one has to carefully maintain a CaO/P_2O_5 weight ratio either below about 0.75 to 1 or preferably above 2 to 2.5 in order to produce cast gypsum with strength properties similar to those made from calcined natural gypsum.

REFERENCES

Beretka, J. 1982. Hydration of calcium sulphate hemihydrate in the presence of phosphoric acid and calcium oxide. J. Chem. Tech. Biotechnol. 32: 607-613.

Beretka. J. and T. Brown. 1983. Hydration of calcium sulphate hemihydrate in the presence of phosphoric acid and calcium oxide: II. Physical properties. J. Chem. Tech. Biotechnol. 33A: 299-308.

Beretka, J. and T. Brown. 1986. Hydration of calcium sulphate hemidydrate in the presence of phosphoric acid and calcium oxide: III. Phosphogypsum. J. Chem. Tech. Biotechnol. 36: 512-518.

Berry, E.E. 1972. Some observations on the setting of calcium sulphate hemihydrate plaster in the presence of phosphoric acid and hydrated lime. J. Appl. Chem. Biotechnol. 22: 667-671.

Ridge, M.J. 1964. Hydration of calcium sulphate hemihydrate. Nature (London). 204: 70-71.

Ridge, M.J., G.A. King and B. Malony. 1972. Reconsideration of a theory of the setting of gypsum plaster. J. Appl. Chem. Biotechnol. 22: 1065-1075.

Wirsching, F. 1978. Lime sensitivity - a characteristic of the hydration of phosphoric-acid-by-product-gypsum. **Matèriaux** et Constructions. 11: 62-64.

ANHYDRITE - POSSIBLE SUBSTITUTE FOR WHITE PORTLAND CEMENT

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ABSTRACT

The gypsum anhydrite, obtained on calcination at about 500°C is the known product. But the gypsum calcined at higher temperatures around 950°C not only attains the crystallographic transformations but also the mineralogical constituents through the solid phase interaction of Al_2O_3, SiO_2 & Fe_2O_3, those lie as impurities in the gypsum. The set product moulded out of this anhydrite has shown the plasticity, colloidal surface, and the capillary action of absorption, during curing, establishing the formation of C_3A & C_2S in addition to C_4AF.

The setting behaviour of gypsum is purely attributable to its crystallographic transformation, from monoclinic to orthorhombic, on calcination, and in the reverse form during hydration:

$$\underset{\text{(Monoclinic)}}{CaSO_4.2H_2O} \quad \underset{\text{hydration}}{\overset{\text{calcination}}{\rightleftharpoons}} \quad \underset{\text{(Orthorhombic)}}{CaSO_4}$$

The setting behaviour of cement is the result of its mineralogical transformations. The four principal mineralogical phases undergo stoichiometric reactions to yield several mineral formations.

As the anhydrite obtained at 950°C contains both crystallographic and mineralogical transformations during setting and hardening, it has been identified and named as 'Crystallo-Mineral

combination of setting behaviour'.

A comparative study has been undertaken to project the anhydrite as a substitute for white Portland Cement (WPC) because of its attaining commandable strength.

Though the anhydrite has developed considerable water repellency, it could not match in this aspect with WPC. Once this insolubility factor is achieved to the anhydrite through further proportions of crystallo-mineral combinations, it can occupy a better marketing place, when compared to WPC, for its comparative low heat consumption and obvious relevant economic factors.

Of all the gypsum grades, Anhydrite I gives the maximum strength. Its slow setting allows the workability comparable to that of Portland cement and hence taking the advantage of its whiteness, it is aimed to project it as a substitute for WPC. To mitigate its characteristic solubility, it is aimed to achieve mineralogical constituents like C_3A, C_2S and C_4AF, within the calcined gypsum, by subjecting the gypsum to calcination at 950°C.

Phosphogypsum, which contains Fe_2O_3 as an impurity tends to add pink colour to the anhydrite obtained on calcination within a temperature zone of 500-750°C (Neville, 1975). While trying to neutralise or vitalise the effect of Fe_2O_3, an exercise has been done to convert the Fe_2O_3 into a mineralogical phase C_4AF. To achieve this, the gypsum was calcined to 950°C. The anhydrite so obtained was not only relieved of its pink colour but was also rendered white with mild lustrousness, showing remarkable gain in strength. In the process, the SiO_2 and Al_2O_3 existing as impurities in gypsum have reacted with the free CaO to form C_3A and C_2S contributing for the insolubility of resultant anhydrite as well rendering surface hardness.

INTRODUCTION

White Portland Cement (WPC) is a product obtainable at a high sintering temperature around 1550°C followed with vitrification. Its production activity is, however, confined because of highly selective involvement of raw material, the iron-free limestone, to avoid colouration to the product. Owing to the above factors, the manufacturing costs prove to be very high, percolating down to the end product price, to result in making the product of premium sector beyond the reach of average income group of housing. Also the limited availability of selective raw material does not allow the industry to grow, thereby leaving a wide gap between demand and supply.

Hence it is desirable if a white cementitious product is developed based on an abundantly available raw material, without sacrificing the whiteness and strength parameters.

Though the Anhydrite I, duly processed and calcined at around 950°C matches to WPC both in strength and grade of whiteness, the characteristic water impermeability of cement could not be attained, on account of various technical reasons, to its desired levels. If this anomaly could be set right, gypsum white cement would certainly score its command over that of WPC, both in price and supply, because of the low process temperatures and abundant availability of raw material respectively.

The chemistry of cement setting confirms that the hydrated compounds of silicates and aluminates of calcium form into a protective coat to the set mass to render hardness as well as water impermeability. Hence the work has aimed to achieve these mineralogical phases for their possible role to enrich the virtues of Anhydrite as a befitting product to replace WPC.

MAIN TEXT

When gypsum was heated to 750°C to produce anhydrite, the product has resulted with pink colouration. The investigations on the product have resulted in the following observations:

i) Complex phosphates and iron compounds are responsible to render pink colour and reduction of strength.

ii) A practical way to remove these compounds is not, available to achieve a white product.

iii) Even with an accelerator of 3%, the setting and strength behaviours are not satisfactory.

To counteract the above anomalies, the following factors of cement chemistry were taken into consideration, before making further progress:

1) The basic colour rendering iron compounds have to be chemically engaged. For this purpose converting the same into C_4AF, through corresponding addition of CaO and Al_2O_3, could render its role as a mineralogical constituent. The ferro cements, which are rich of this mineralogical phase are good hydraulic binders, and hence it is expected that this achievement of mineral phase in gypsum would not only neutralise the ill-effect of iron compounds but also, contribute in a positive way for strength.

2) The presence of P205 content upto 1.5%, during the sintering stage of mineralogical formations, gives raise to a cement with high 28 days strength as indicated in Table I (Chemie Linz AG, 1976).

TABLE I

P_2O_5 in clinker, %	2	1	0
Compressive strength, kg/cm^2 :			
After 1 day	70	100	120
After 3 days	190	200	220
After 7 days	250	320	320
After 28 days	420	450	400

3) when gypsum is heated to 950°C, in order to achieve the conversion of iron to C_4AF, it is the same temperature for the formation of C_2S, and hence the silica in the

form of SiO_2, remained as impurity in the gypsum, reacts with free lime and forms into C_2S. In general, the formation of C_2S is in two forms, alpha and beta, where the former one is non-hydraulic and the latter one is strongly hydraulic. The presence of P_2O_5 in its low levels below 1.5% contributes for the formation of β-C_2S (Welch & Gutt, 1960 and Gutt & Smith, 1971) that renders greater 28 days strength comparable to that of C_3S.

While achieving the neutralisation of effects caused by phosphates and ferrites in the above stated manner, it is expected that the resultant anhydrite would respond with positive strength and setting behaviours.

TESTING PROCEDURE :

i) A study of 'Differential Thermal Analysis (DTA)' on the product to locate the mineralogical transition zones by means of DTA curve and correlate it with the temperature curve to determine the temperature zone (Fig.1).

ii) With reference to the temperature zone identified by means of DTA, conduct the calcination of phosphogypsum, duly refined and added with corrective ingredients, to the prescribed temperature.

iii) Size reduction of the calcined product to the possible fineness by means of grinding.

iv) Preparation of test cubes in standard size of 125 cm^3, curing the same by wrapping with wet cloth, and testing the strengths.

The samples tested for strengths have shown the following results as in Table II.

TABLE II

	Sample I (with no admixtures)	Sample II (with corresponding CaO and Al_2O_3 for C_4AF formation)	White Portland cement
1. Calcination temperature	750°C	950°C	Not known
2. Colour of product	Pink	White with mild lustre	white
3. Setting time : mnts			
Initial	60	30	40
Final	330	240	420
4. Consistency factor	0.22	0.16	0.33
5. Density of set product gm/cc	2.12	2.2	1.86
6. 28-day strength kg/cm^2	372	528	456

STOICHIOMETRY DURING CALCINATION :

The formation of C_3A, C_2S and C_4AF have taken place between 850-950°C. The availability of alumina and ferrite phases has worked as a flux and achieved the formation of these mineral phases more positively within these temperature zones (Taylor, 1981). The P2O5 content available in the gypsum has contributed for the formation of β-C_2S.

SETTING AND HARDENING BEHAVIOURS OF THE ANHYDRITE :

The product obtained as sample II has shown remarkable plasticity, on addition of comparatively less amount of water, and also set faster resulting in a high strength product over sample I. Hence, sample I is discarded and sample II is further studied for its behaviours and correlated with the following salient theories of Portland cement.

Low consistency factor:

In comparison to the factor of 0.33 to WPC, 0.16 to the anhydrite is a remarkable phenomenon. For any cementitious product, the lower the consistency factor the greater is its set density to result in higher strengths. In view of this fact, for the preparation of high strength concrete Sodium chloride or calcium chloride, not exceeding to the level of 2%, is added which is of course confined to 1.5% max. according to the British Standard CP 110: 1972.

In the present case, the low consistency factor can be attributed to the presence of alkalis and chlorides in the range of 1.0 to 1.5%, as the impurities carried into the phosphogypsum, those could not be volatalised because of process temperature below 1000°C. To discuss the reactions in brief, the above stated compounds create some electrolytic reactions, on addition of water, the result of which are more evident in the presence of C_3A, based on the investigation of Candlot (Bogue : p.417, 1947).

Ultimately, due to the internal surface reactions, the matrix reaches to the thixotropic point at minimum level of water availability resulting in the low consistency factor to yield a denser mass with reduced setting durations.

Colloidal theory & plasticity :

When the material is cast into the mould and the upper surface is trowelled for evenness, the mass has shown a typical plasticity which is a characteristic for WPC also. This plasticity is the typical phenomenon for rendering workability on the matrix which is a result of the colloidal formation in the product (Bugue : p.360-61, 1947). The anhydrite also exhibited the same phenomenon of plasticity thereby confirming in its constitution, the existence of compounds contributory for the colloidal formation.

The colloidal theory contains series of observations and voluminous interpretations which could be presented in a nutshell as follows, to interpret with the constituents and behaviours of anhydrite (Bogue : p.358-59, 1947).

“A strong, water impervious cement stone results mainly due to the formation of hydrogels of silicates, aluminates and ferrites, where the silicates play a major role. The action of water on cement bring about the solution of lime, aluminates, sulfates and other compounds of cement. From this solution there are precipitated various crystalline products as calcium aluminates, calcium sulfoaluminate, calcium sulfate, and calcium hydroxide. This gives a material possessing some strength but not at all resistant to disintegration upon action of the water. Water will easily penetrate and soften it. The colloid forces now come into play. As soon as the lime water has reached a definite concentration, it acts on the calcium impoverished silicates, through electro-chemical forces, and forms the hydrated calcium silicates. Because of the difficult solubility of the silicate, it forms into a gel, a colloidal state, which fills the pores of the cement and makes the latter impermeable to water. The gel is soft, but the inner crystalline mass of the cement eagerly withdraws water from the gel and in that way the gelatinous surface becomes hard. The greater strength and water resistance of the cement are thus explained as due almost entirely to this gel formation and its drying out due to the capillary action of inner crystalloids".

In support of the belief about the colloidal formation for anhydrite, the cubes have shown constant strength gain on curing, during hydrolysis, when they were wrapped with wet cloth through day to day watering.

In order to confirm the colloidal effect with the analogy of setting behaviour of resultant anhydrite, some set cubes were dipped in water after the completion of final setting. After two to three days, the cubes were surrounded by a thick fog like structure of viscous material. Then the cubes were taken out and washed off of the colloidal structure and dipped into fresh water again. After the removal of colloidal film from the set anhydrite before it was allowed to set hard in the dry conditions, the cubes have shown marked deterioration and disintegration of set particles upon immersion in the water.

Crystalline theory and hardness :

In 1887, Le Chatelier succeeded in discovering and postulating various points on this theory, which are acknowledged worldwide even today, to identify the setting of cement (Bogue : p.350-56, 1947). Accordingly the whole. process of cement setting has been identified in three distinct phases:

a. The chemical phenomenon of hydration;
b. The physical phenomenon of crystallisation and
C. The mechanical phenomenon of hardening.

The hardening of anhydrite can be referred to the above three phenomena and parallels could be drawn:

The dehydrated or anhydrous crystals of cementitious products, upon hydration, take up the water with such an avidity which results in rapid transformations of crystals leading to the interaction and entanglement with enlarged crystal phases to give rise to hard mass.

The hydration is simultaneously accompanied with the formation of crystalloids. In a solution which is just saturated, crystallisation cannot take place. But, if some change in conditions of the solution & solvent is obtained whereby a temperary meta-stability or super saturation is obtained, then equilibrium is established to the solvent which is followed by precipitation where the precipitate is the required crystalloid for hardening. The heat of hydration acts as the force to achieve this metastability or supersaturation. this is where the chemical phenomenon and the ultimate exothermic reaction of anhydrous cement products come into picture, rendering the necessary force for the attainment of supersaturation and the ultimate formation of crystalloids. Le Chatlier found that crystals precipitating from highly super saturated solutions were frequently developed or enlarged along the principal axis to abnormal dimensions, resulting in 'long, extremely slender prisms, true threads whose length may exceed one hundred times to their thickness'. These usually grow in spheurulic form about nucleus. This condition was found to be true of many salts, including gypsum anhydrite, which normally crystallise with equal dimensional development in all directions.

The dihydrated gypsum crystals are monoclinic and the anhydrited gypsum is orthorhombic in its crystal form. According to Desch & Davis it is the transformation of crystallography in Anhydrite from rhombic to monoclinic structure, upon hydrolytic reactions, with enlarged surface expansion of its faces leading to a large needle shaped slender prisms, contribute for the hardness in it (Bogue : p.363, 1947). In cement minerals it is the internal chemical reactions of mineral constituents leading to numerous compounds of solutes during hydrolysis resulting in the crystalloids of various shapes, dimensions and surfaces, that contribute for the hardness.

In the Anhydrite sample about 88% of the material was in its orthorhombous crystalform whereas about 12% has resulted with mineralogical formation of C_2S, C_3A and C_4AF. It is the combined hydrolysis and transformation of these crystals and mineral forms that have rendered the strength to the anhydrite, more than that of WPC, which has initiated the authors to identify and name it as “Crystallo-Mineral combination of setting behaviour”.

The support the improved characteristics of gypsum, on attaining the crystallo-mineral combinations, another case can be cited.

M/s Salzgitter Industriebau of West Germany have developed weather proof panels adding specific doses of flyash to calcined gypsum added with other admixtures. These panels proved to be consistent in their strength in dry condition as well as in wet condition, even on absorbing water, which is an unusual phenomenon for a set product of pure gypsum.

The authors take the initiative to say that the cited weather proof panels maintained their strength, even in their wet condition, because of their distinctive set behaviours, attained in the presence of mineralogical constituents those were available through the addition of flyash. To elaborate it forther, it has to be mentioned that the strength and hardness of a cementitious matrix depend upon the cohesion within the crystals themselves and the adhesion between the individual crystals, and between these and other aggregate bodies present therein (Bogue : p.357, 1947).

Since cohesion is regarded as a specific property of each crystalline material, the maximum ultimate strength of pure gypsum matrix is limited by the cohesive forces of that particular crystallography. This is where the mineralogical constituents are recommended to play their role. The chemical reactions of the minerals and the resultant compounds give rise to the activity of adhesive forces for the crystals to adhere to one another or to bind the aggregates within them. Thus, it is to be pointed out that the addition of sand to gypsum plaster is not virtuous to render an accountable strength while lime silicates are at advantage to be mixed with sand for a stronger matrix.

This furtherly allows the authors to conclude that, gypsum, in association with mineralogical constituents, either through addition or processly developed, sheds its characteristic anomalies like fall, in strength and solubility to give raise to a new phenomenal product befitting to be used in the place of cement.

Fineness :

Apart from the qualitative and quantitative mineral constituents of cement, fineness has also its say to contribute towards the strength of the set matrix. The finer the particles of the cement the more the surface contact with water and the higher the crystalloid formation leading to the ultimate strength. It is observed that an increase in unit surface area of cement by 1000 cm^2/gm over its normal fineness raises its activity by 20 to 25% (Komar, 1979). This gain in strength can be attributed to the attainment of adhesive forces between the particles where the forces are high as much the cement is fine.

The fineness of the cement has relation with porosity also. The more the fineness of cement the less the pores in setting mass.

the anhydrite obtained on calcination was retained by 20% on 100 mesh B.S. sieve which has resulted in a 28-day strength of 240 kg/cm^2. On ground to pass 100% through 150 mesh B.S. sieve the same anhydrite has yielded a strength of 528 kg/cm^2 on 28-day, proving the gain in its strength through the attainment of adhesive forces between the particles, owing to the more surface contact and higher crystalloid formation, in direct relation with the increase in its fineness. It has also been observed that the water consistency factor is inversely proportional to the fineness of the anhydrite, to result in a denser mass for ultimate gain in strength.

The anhydrite resulted with the strength of 528 kg/cm^2 was ground in a domestic grinder and could not attain the grade fineness of portland cement. If this parity can be achieved, the resultant anhydrite could develop the strength much above to 600 kg/cm^2, establishing a record of the product.

CONCLUSIONS

The anhydrite obtained for this study constituted with mineralogical formations to about 12 to 14%, the balance being anhydrite in its orthorhombic crystal form. In spite of this low availability of mineralogical constituents,the product has shown remarkable cementitious behaviours in parallel to that of white Portland cement. The setting behaviour out of combined transformations of crystallography in anhydrite and mineralogy of other constituents could be attributed to the phenomenal strength development which has inspired the authors to identify it as 'THE CRYSTALLO-MINERAL COMBINATION OF SETTING BEHAVIOUR'. They throw open the further studies, with critical analyses on X-ray differaction and crystallography, for the identification of absolute contributory constituents in order to increase their quanta in anhydrite to the effective proportions, during the process of calcination, to achieve an acceptable product as a worthy substitute for white Portland cement.

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REFERENCES

Bogue, R.H. 1947. The Chemistry of Portland Cement. New York : Reinhold Publishing Corporation.

Chemie Linz, October, 1976. Private Communication to The British Sulphur Corporation Ltd.

Gult, W. and Smith, M.A. 1971. Cement Technology, Volume 2, No.2, March/April pp.41-50 and No.3, May/June pp.91-93.

Komar, A. 1971. Building Materials and Components. Moscow, MIR Publishers, p.149.

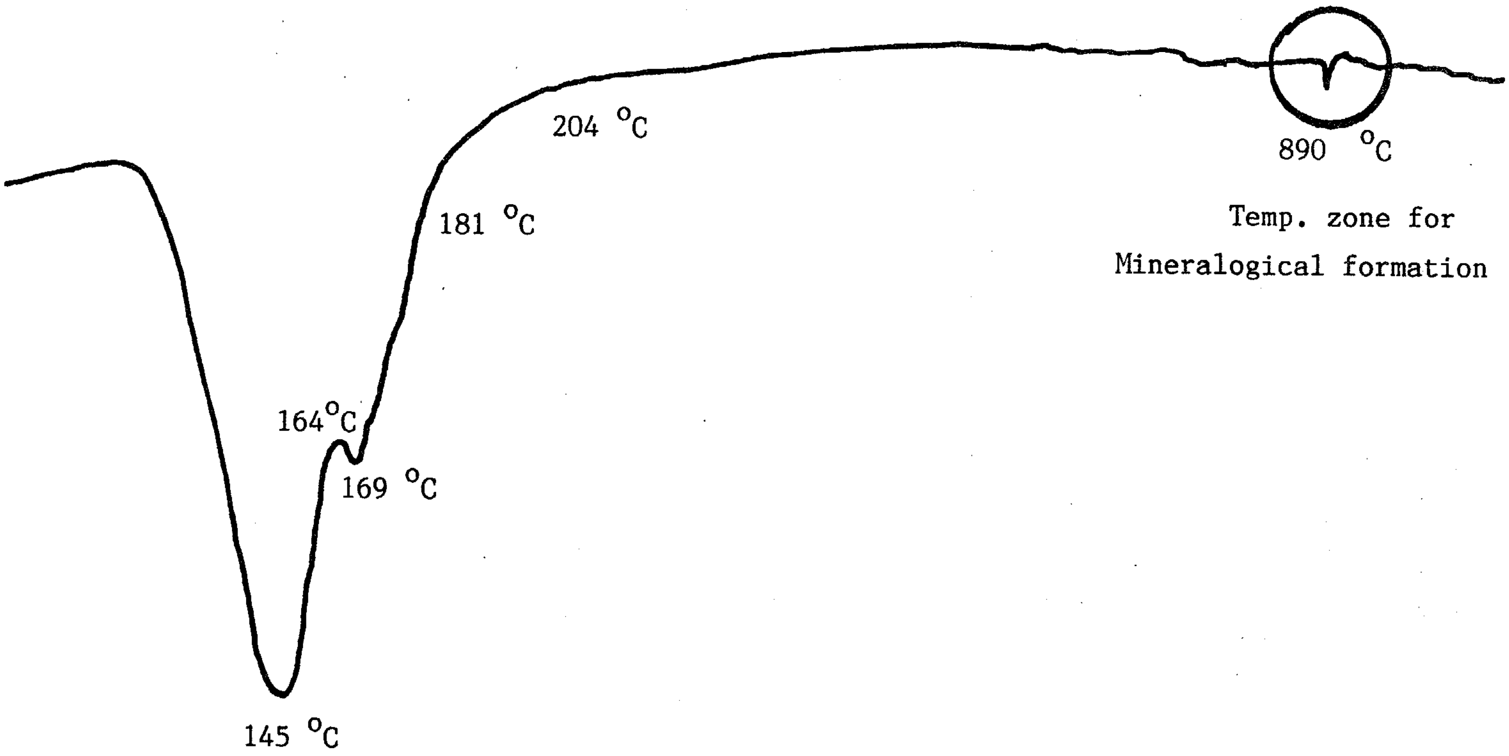
Neville, A.M. 1975. High Alumina Cement Concrete. New York. John Wiley & Sons.

Taylor, H.F.W. 1981. The Chemistry of Cements. London & New York. Academic Press. p.101.

Welch, J.W. and Gult, W. 1960. The effect of minor Components on the hydraulicity of the Calcium Silicates. Paper presented at the Fourth International Conference on the Chemistry of Cement, Washington D.C.

FIGURE 1

DTA CHART ON PHOSPHOGYPSUM WITH CONSTITUENTS FOR MINERALOGICAL FORMATION



PLASTER REHYDRATION STUDIES AND THEIR PLAUSIBLE USE IN THE ECONOMIC CONVERSION OF CALCINED PHOSPHOGYPSUM INTO BUILDING MATERIALS

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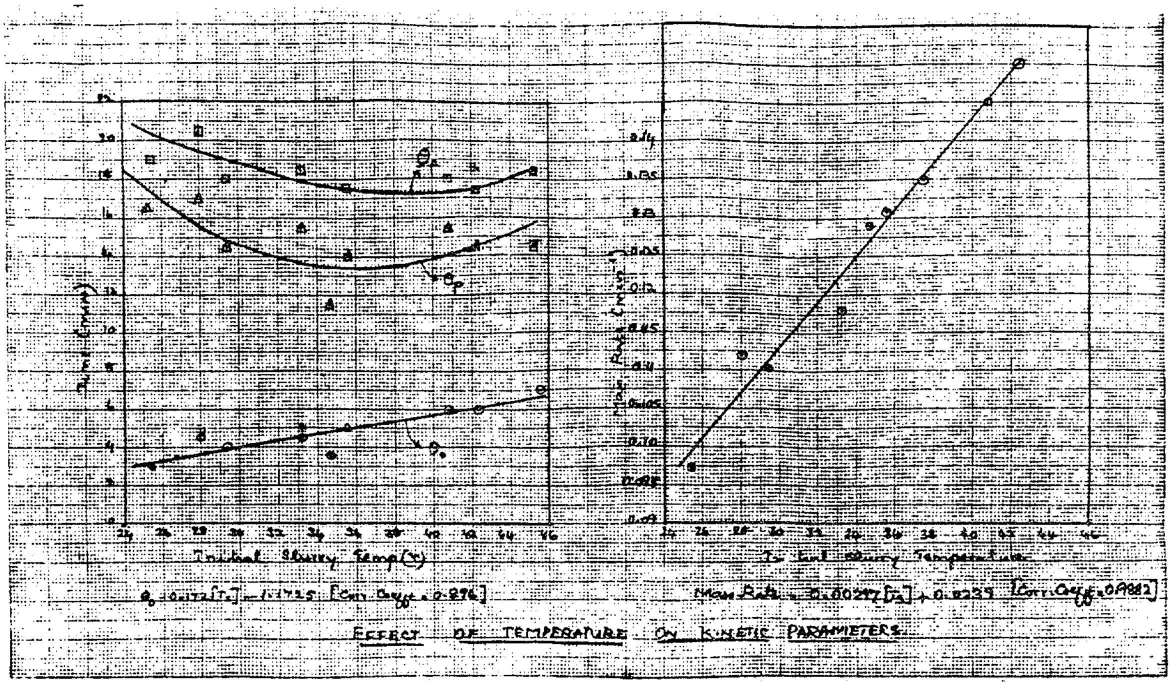
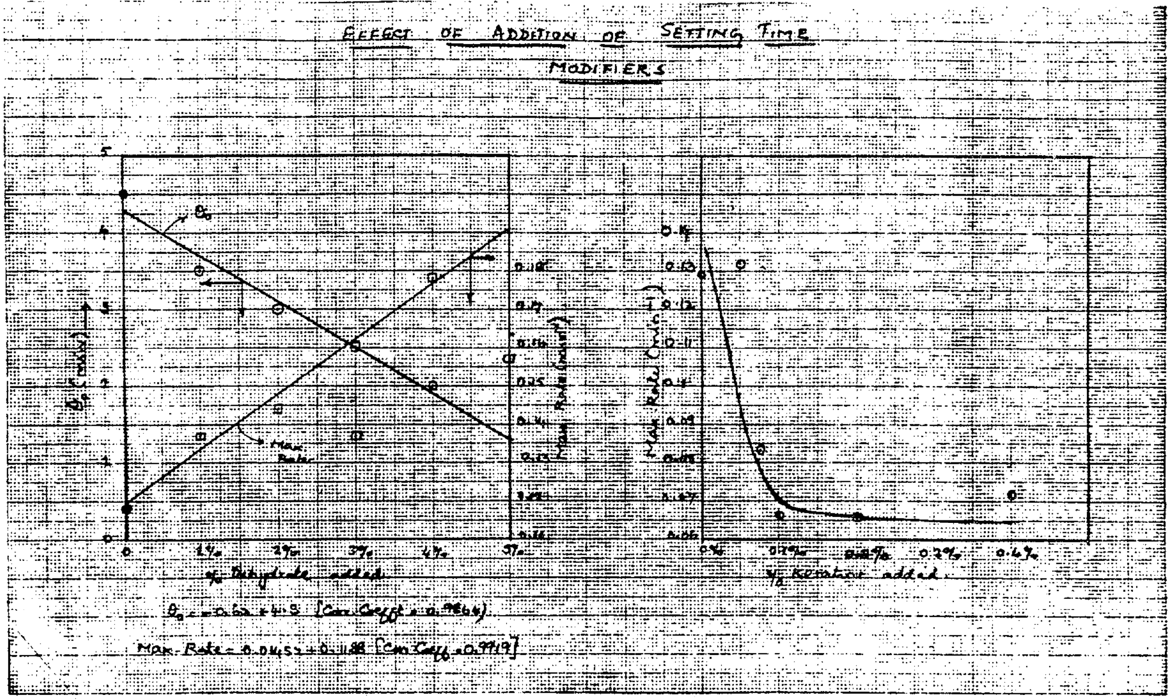
There has been an increase in the availability of phosphogypsum over the years, but this is not reflected in the growth of its utilisation, especially in developing countries. The conversion into building materials can be made increasingly attractive by improving the economy of operation. One possibility is to make lighter castings of acceptable physical properties resulting in direct savings in plaster consumed and indirect savings in construction cost. This can be achieved by choosing proper calcining route and optimising the operating conditions. This condensed paper summarises the optimisation of grinding requirements using plaster obtained through two different calcination routes; viz. pneumatic calcination process and tray drier. Phosphogypsum containing 20.09% crystalline water, 32.4% CaO; 45.24% SO_3; 0.29% T.P_2O_5; 0.124 % ws P_2O_5; 0.783% T.F.; 0.13% WSF; 0.628% organic matter and 0.44% acid insoluble was used for all trials. Pneumatically calcined plaster was ground in a hammer mill whereas stucco prepared in the tray drier was ground in a ball mill.

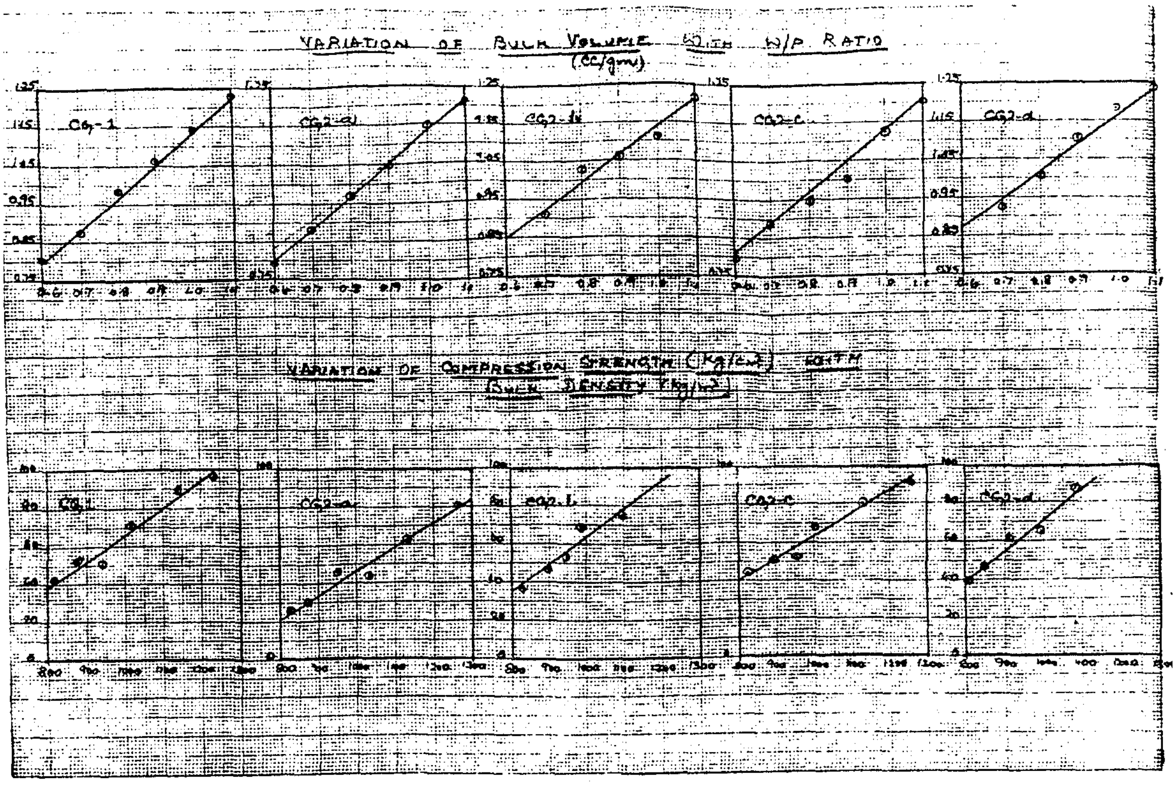
The adequacy of workability of pneumatically calcined plaster was confirmed by evaluating the kinetic parameters, viz. the periods of induction and influxion (θ_0 and θ_p)





Figs. 1, 2, 3 & 4

and the maximum rate during rehydration, for different initial slurry temperatures (25°C to 45°C) and percentage inclusion of setting time modifiers (% dihydrate and % keratine). These are presented in Figs. 1 to 4.



Figs. 5 & 6

Similar studies were carried out using plaster calcined in a tray drier. The results were similar except that the maximum rate was marginally lower.

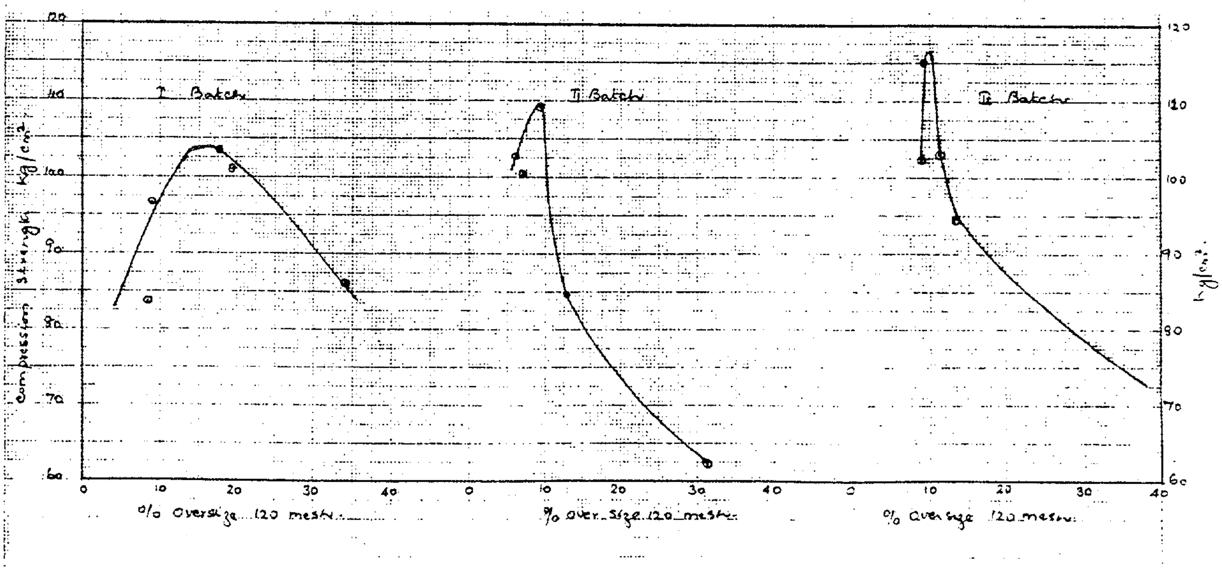
Grinding had only marginal effect on θ_o and θ_p ; but with increasing residance time in the mill, the rate of rehydration increased to a maximum of 0.149 min^{-1} registering a slight decrease thereafter. Four samples (CG2a-unground; CG2b-ground with minimum residance time; CG2c-ground with optimum residance time and CG2d-ground with maximum residance time) were generated out of pneumatically calcined plaster. CG1 and CG2c were duplicate samples. Castings were made with different water/plaster ratios (0.6 to 1.1) and their compression strengths tested. The results are presented in Figs.5

and 6. The relationships between bulk volume and W/P ratio and that between strength and bulk density were found to be linear with a high degree of correlation, for all cases.

These correlations were used to predict, in each case, the limiting W/P ratio to be used for casting so that a desired compression strength, viz. 50 kg/cm^2, can be achieved. The summary is as follows.

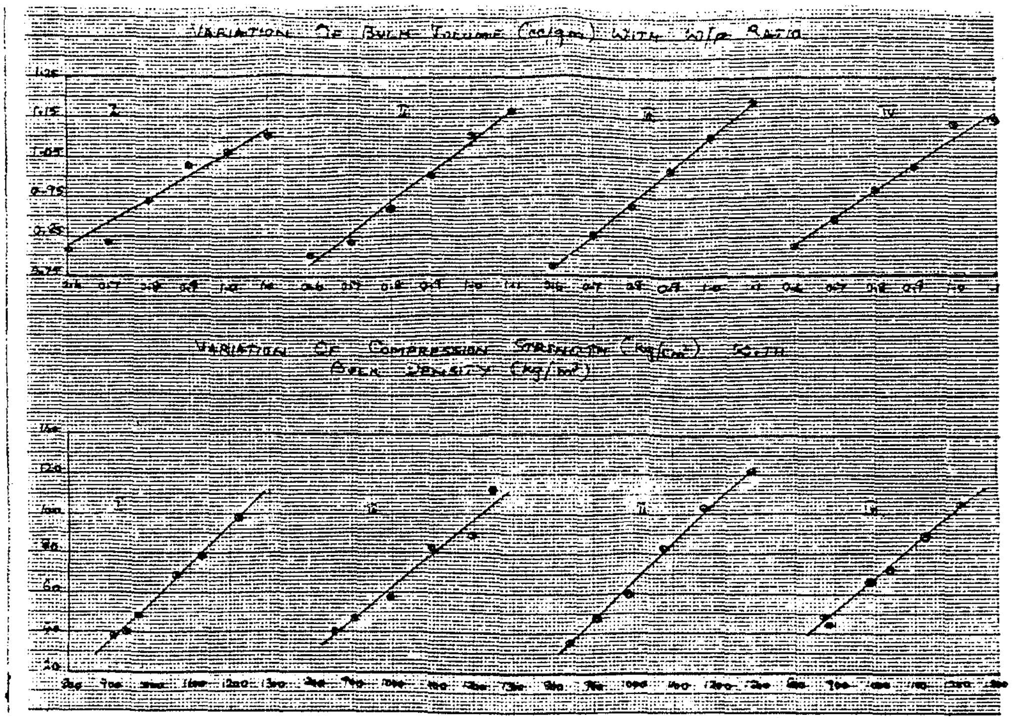
Sample No.	Limiting values of castings		
	Bulk density Kg/cu.m.	Bulk volume cc/gm.	W/P ratio
CG2a	1026	0.975	0.81
CG2b	905	1.104	0.95
CG2c	) 879	1.137	1.00
CG1	) 877	1.141	1.00
CG2d	867	1.154	0.975

Similar studies were conducted using plaster calcined in tray drier. The results are presented in Figs 7 to 10.



VARIATION OF COMPRESSION STRENGTH WITH PARTICLE SIZE

Fig. 7



Figs. 8 and 9

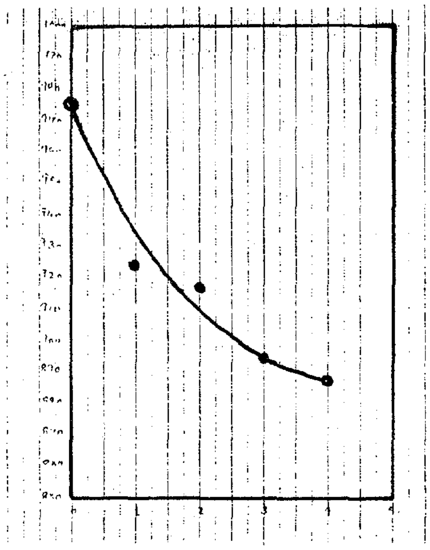


Fig.10

The relation between particle size and strength is shown in Fig.7; the correlations similar to Figs.5 and 6 are shown in Figs.8 and 9 and the limiting bulk density is plotted against hours of grinding in Fig.10. The data presented in the condensed paper indicates the existance of an optimum grinding requirement, the judicious use of which can lead to nearly 15% reduction in plaster consumption.

The calcining method did not have any effect, for the type of products chosen for this study.

PURIFICATION AND PRODUCTION PROCESSES

LOCATION OF RADIUM IN PHOSPHOGYPSUM AND IMPROVED PROCESS FOR REMOVAL OF RADIUM FROM PHOSPHOGYPSUM

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ABSTRACT

During the first International Symposium on Phosphogypsum, I had the opportunity to describe a way of reducing uranium content, and then radium content of phosphogypsum, from 9 to 7 pCI/gram by hydrocycloning treatment of phosphogypsum.

We were not able to go below this level of 7 pCI/gram.

In order to understand this fact, we started a study on the location of radium in phosphogypsum. At such a low level of radioactivity, the search was difficult. Finally, by using KOKAK LR 115 films as an α radiation detector on a sample of the overflow stream of a hydrocycloning treatment which-concentrates radium to the overflow stream, we were able to locate the two main sources of α radiation in phosphogypsum :

- crystals of Calcium, Strontium, Baryum Sulfate which are very rich in co-crystallyzed Radium with a diameter from 4 to 8 µm,
- deposits of very small particles of 1 µm size stuck to the surface of Calcium Sulfate crystals which are not eliminated with the overflow of the hydrocycloning treatment.

This result enabled us to find two processes with the potential to eliminate the major, part of the radium contained in phosphogypsum by hydrocycloning-treatment:

- one during the chemical attack of phosphate by sulfuric acid,
- one by retreatment of existing phosphogypsum.

The main problem left is the disposal or treatment of the produced waste with a 600 pCI α radiation per gram of waste.

INTRODUCTION

During the first International Symposium on Phosphogypsum in November 1980, I described a way of removing part of the radium entrapped in phosphogypsum by hydrocycloning of the phosphogypsum slurry obtained from repulping of the cake produced by the filter of a phosphoric acid plant (Fig. 1).

The hydrocycloning treatment in the installed equipment removed most of the minus 20 µm particles, and roughly two-thirds of the radium responsible for this a radiation emission.

The a 226 Ra radiation emission from phosphogypsum, collected at the underflow, was reduced from 35 to 13 pCI/gram while the α emission from the overflow product was increased from 35 to 480 pCI/gram. You can see the type of installation used for this test.

At that time, we had hoped to reduce the radioactivity of the underflow pulp to 7 pCI/gram by putting it through several stages of hydrocyclone treatment (Fig. II).

The test was a failure ; we had no real improvements.

We obtained the desired result by adding a tank with high turbulence between hydrocycloning stage 1 and hydrocycloning stage 2 (Fig. III).

The addition of a second stage of high turbulence did not decrease the *a* radioactivity of the final product. It appeared that with the type of phosphogypsum we were using, hydrocycloning, even combined with a high turbulence agitation tank, reached its limits and was not able to reduce radioactivity below 7 to 8 pCI/gram.

At the end of 1982, we decided to try to locate the remaining radium in order to know if there was a chance to remove it and how this could be done. The first aim was to locate the radium. The second aim was to see the sites where radium was entrapped.

HOW TO LOCATE RADIUM PARTICLES

First, we tried to find radium in standard phosphogypsum with a Scanning Electronic Microscope with secondary electron emission analyzer. We failed.

We thought that the radium particles were too scarce and decided to try to locate them by another means , and then to inspect these sites with a Scanning Electronic Microscope.

Nissan Process

200 T P_2O_5/day

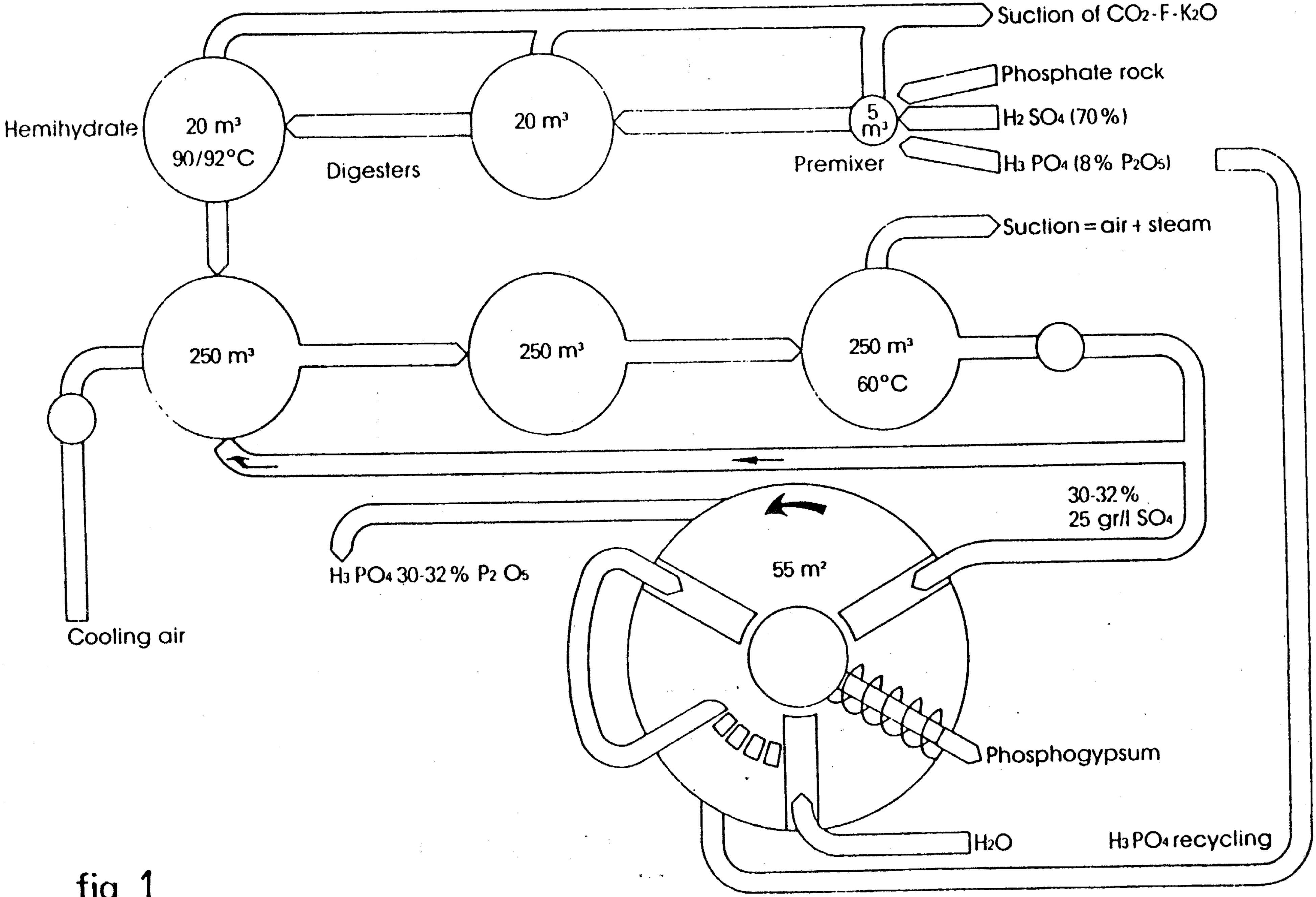


fig 1

Hydrocycloning of slurry

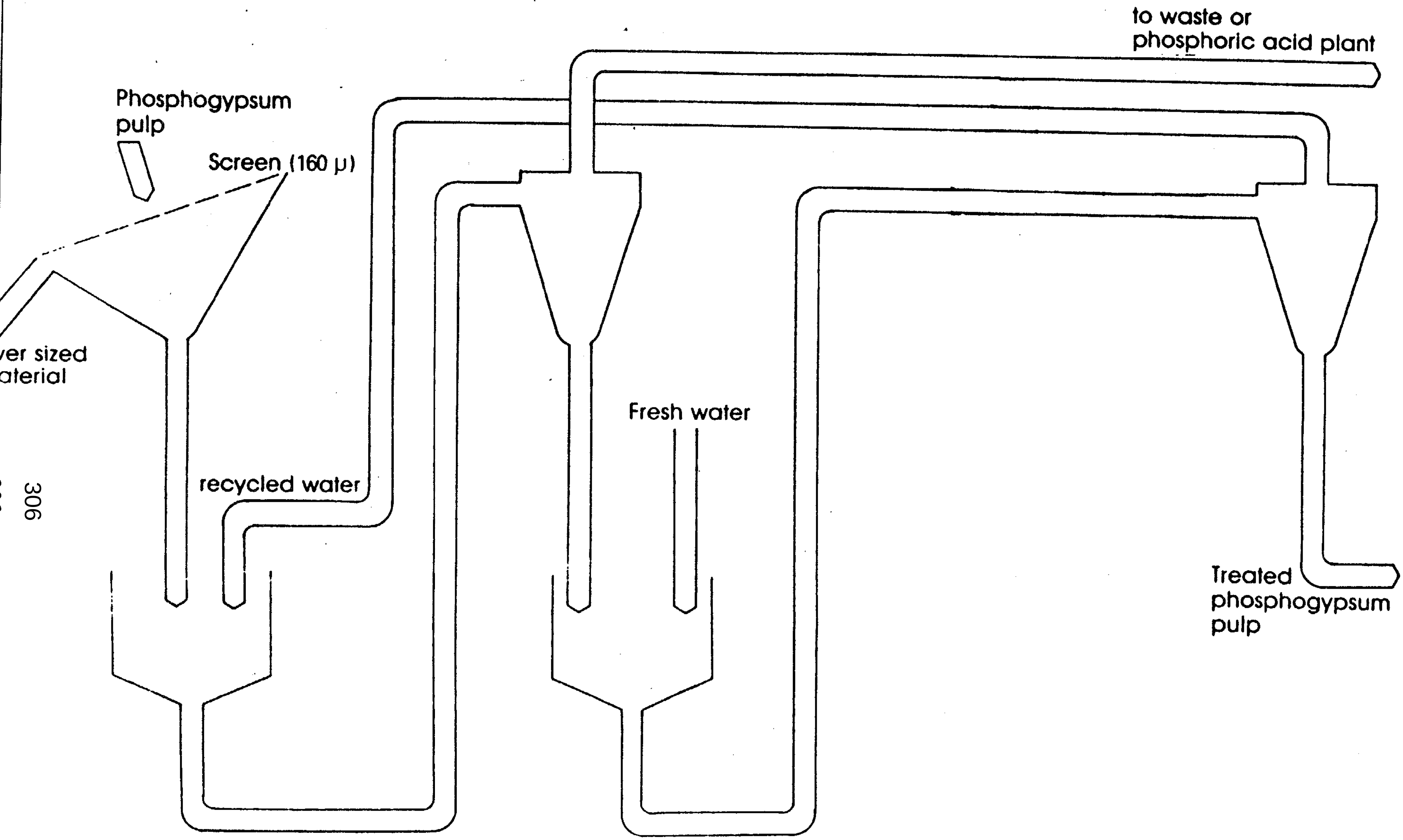


fig 2

Hydrocycloning of slurry

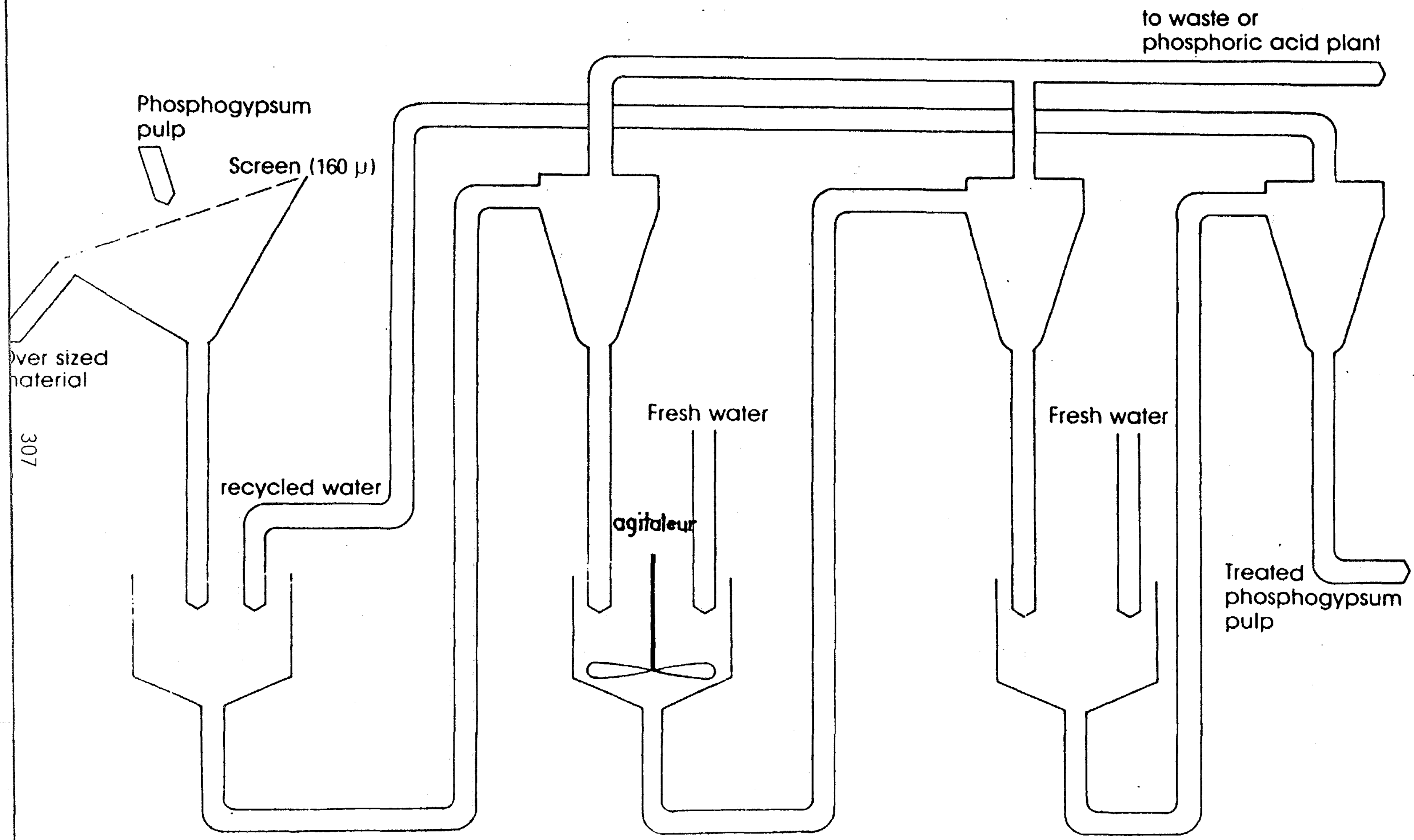


fig 3

It is known that the KODAK Co. sells a special film (the K 115) for detection of sites or sources of α radiation. After exposure of the film for 7 days, we obtained the picture as shown on Fig IV :

- the small points correspond to a few emissions during the week,
- the stars correspond to a spot where a highly radioactive particle giving an α emission is located.

Then, we tried to use this test on two samples :

- one was taken from the underflow of the hydrocyclone : it had a 7.6 ± 1.2 pCi/gram 226 Ra radiation emission.
- another one was taken from the overflow of the hydrocyclone : it had a 480 ± 24 pCi/gram 226 Ra radiation emission.

With the sample from the underflow of the hydrocyclone, we got no impact the film. This fact indicates that the sources able to give an α radiation emission in the treated phosphogypsum are very scarce or that their emission is very weak.

With the sample from the overflow of the hydrocyclone, we got about ten impacts but no star. This number of impacts is in line with the possible radiation emission of the measured radium contained in our sample.

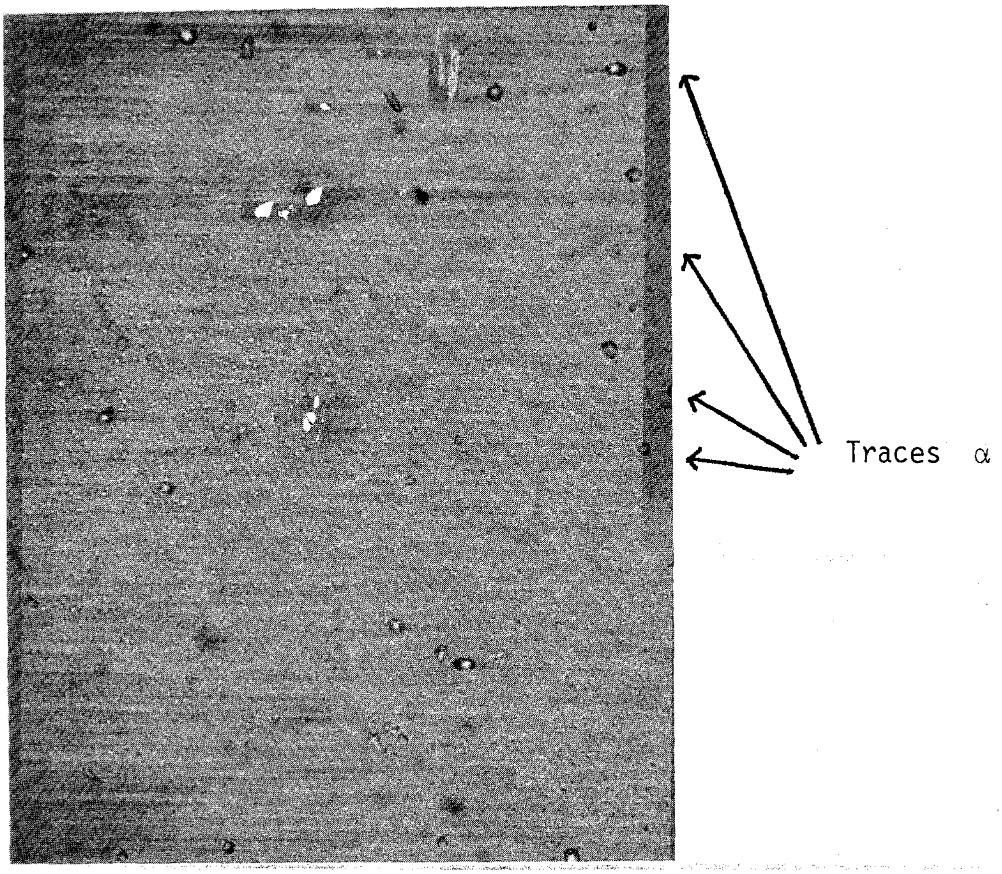
We tried without success to relocate the detected points and to analyze the particles located in these points with a Scanning Electronic Microscope with secondary electron emission at very low energy. It was not possible to relocate the sites which had been detected with the KOKAK film.

At this point, somebody thought to use a Scanning Electronic Microscope equiped with an X ray analyzer. A picture can be obtained with back scattered electrons obtained by the impact from the X ray source. This picture gives a good contrast thanks to the difference between emission from high atomic number elements (as Radium) and emission from Calcium, Oxygen, Sulfur. The result is seen in Fig V.

Then, it was easy to do an analysis of the bright areas, without moving the sample.

It was possible to detect an average of 10 bright spots in a .1x.2mm area.

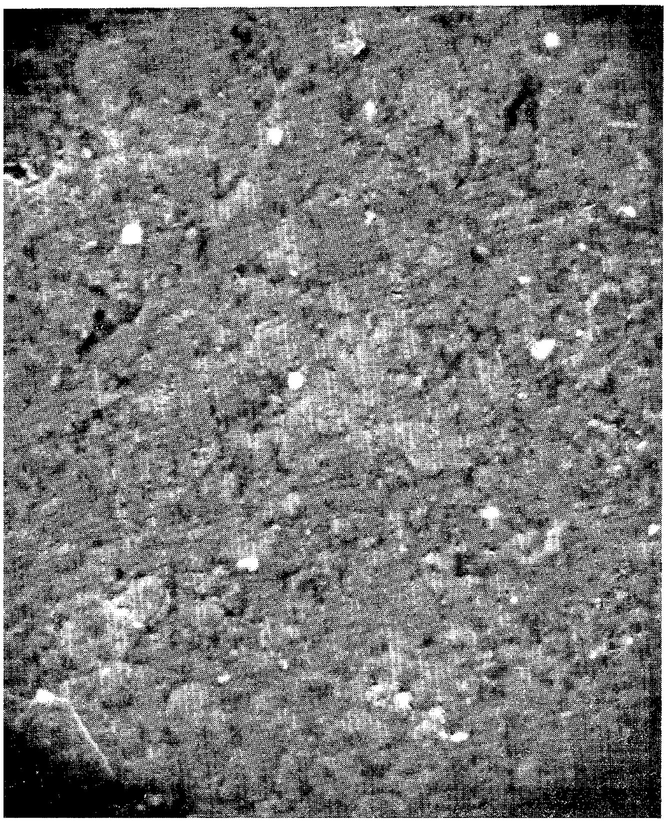
The analysis gave :



X 340

White points are α radiation emission sites
KOKAK LR 115 - type I film (7 days exposure)

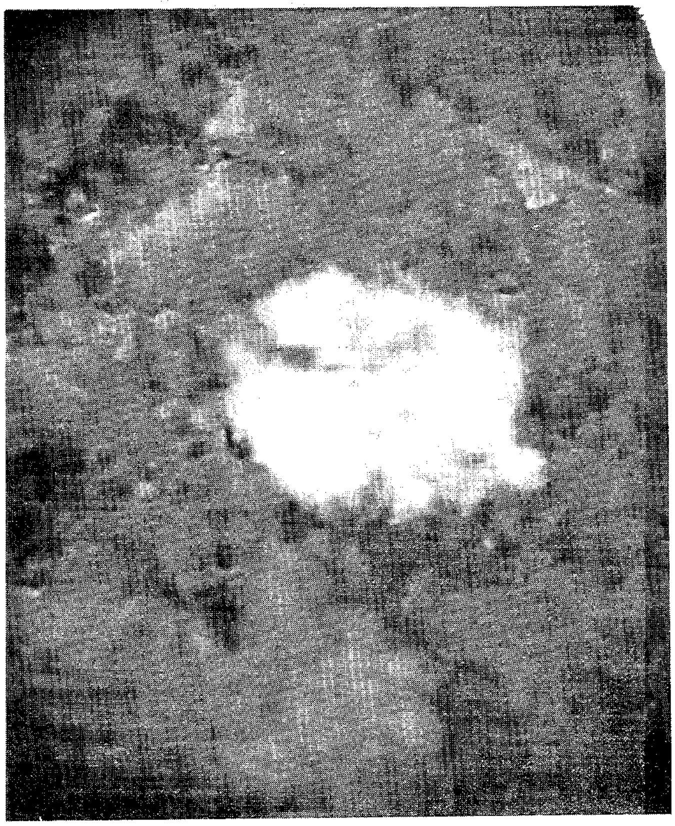
Fig. IV



X 800 10 μ

Fig V a

White points are α emission sites



X 5000 2 μ

Fig V b

White zone is a Ba Ca Sr sulfate zone with high α radiation emission

Fig. V

- No Uranium or Radium phosphate,
- No Radium sulfate,
- Trace of Iron,
- Trace of Calcium and Zinc phosphate,
- Co-crystallized Barium and Strontium sulfate.

Among the components found, there are no naturally radioactive products. Strontium can be made artificially radioactive ; but, in this case, its emission is a β radiation emission and not an α radiation emission.

Since, it is not possible to locate Radium with a Scanning Electronic Microscope, the question of the location of the Radium was left without an answer. However there was a good chance to find it close to co-crystallized Calcium-Barium and Strontium sulfates, sites which were emitting α radiation.

HYPOTHESIS

Looking at the literature, we found that many studies were done by Marie CURIE, O. HAHN, V. KHLOPINE and their research teams regarding salts with which radium can co-crystallize.

At that time, the studies were done to find a way to extract radium. The result was rules to be followed in order to obtain co-crystallization with Radium. These rules are important as they provide the opportunity to capture or to disperse Radium.

All the Radium salts co-crystallyze with Barium salts. This is noted in a GIULINI patent. Also, most of the Radium salts co-crystallyze with the Strontium salts and if we consider Strontium sulfate, in particular, the increase in concentration D is very high. If we call the house crystal "sponge salt", we can write :

$$D = \frac{\text{Radium quantity}}{\text{Sponge salt quantity}} \;\text{(crystal)}\; . \;\frac{\text{Sponge sal quantity}}{\text{Radium quantity}} \;\text{(solution)}$$

D for Strontium is higher than D for Barium and B. GOLDSCHMIDT proposed the use of Strontium salts rather than Barium salts as "Radium sponges".

Finally, the potential content of Radium in Calcium-Barium-Strontium sulfate is between 10 and 100 p.p.m. This amount explains why it was not possible to detect Radium with a standard Scanning Electronic Microscope ; it was too small. On these bases, we considered that the Radium was located with Strontium and Barium.

CONFIRMATION OF RADIUM LOCATION

As mentioned before, we tried to see the sites where Radium is located with a Scanning Electronic Microscope. A test with the underflow of a hydrocycloned sample gave no result. Below 10 pCi/gram the chance to see a site is very remote.

Taking pictures of samples of an overflow of hydrocycloned sample gave good pictures of two types of sites where co-crystallized Calcium-Barium-Strontium sulfate crystals are concentrated :

- small easy to identify balls with a 4 to 8 µm diameter (Fig. VI),
- very small particles (1 µm size) stuck to other crystals (Fig VII).

This explains quite well why treatment by hydrocycloning is able to reduce the radioactivity from 30 to 10 and even to 7 pCi/gram if you are treating the slurry with violent agitation. The small balls are eliminated by the hydrocyclone which is adjusted to get everything below 20 µm as an overflow. The high turbulence treatment pulls up some of the fine particles which are stuck to the big crystals. These particles are eliminated by the second stage of hydrocycloning. All the remaining Radium stays stuck to the big crystals.

It was not possible to determine the exact composition of the small 1 µm particles stuck to the other crystals, but it appears that the composition of the small ball is some type of good Radium absorber.

If tie can increase the number of small balls, we should have more Radium absorbed by these balls, and we should be able to eliminate more Radium by the hydrocycloning process. If we have enough balls, we should expect to be able to extract all the Radium present in the slurry.

IMPROVED METHOD FOR RADIUM REMOVAL FROM PHOSPHOGYPSUM

The next step was to know the exact composition of the small balls. The analysis by the X ray diffraction analyzer of the Scanning Electronic Microscope gave the following (Fig VIII) :

- Al_2O_3	3 %
- SiO_2	10
- K_2O	0.4
- SO_3	37
- CaO	14
- BaO	30
- SrO	5

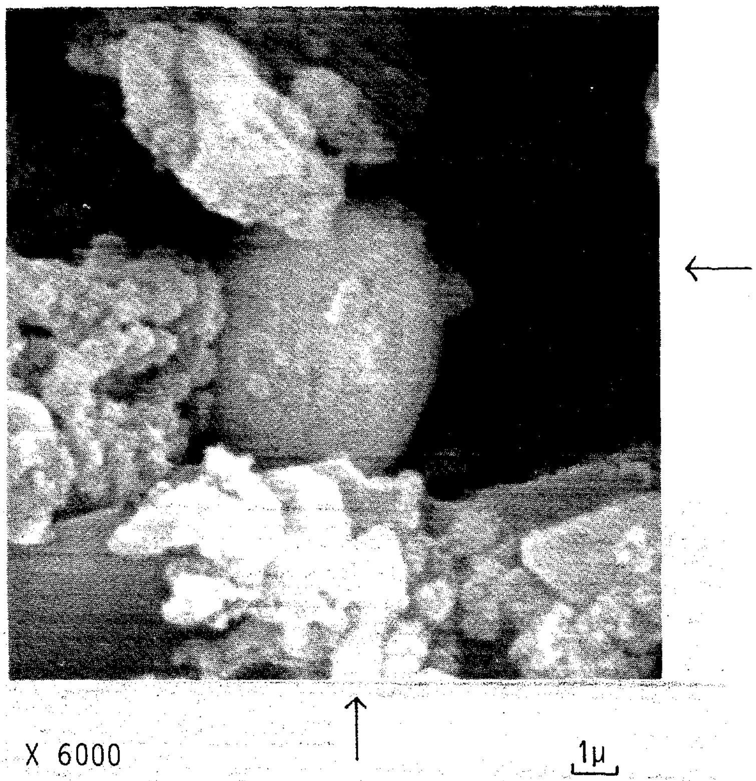


Fig. VI Ca, Ba, Sr sulfate (ball)

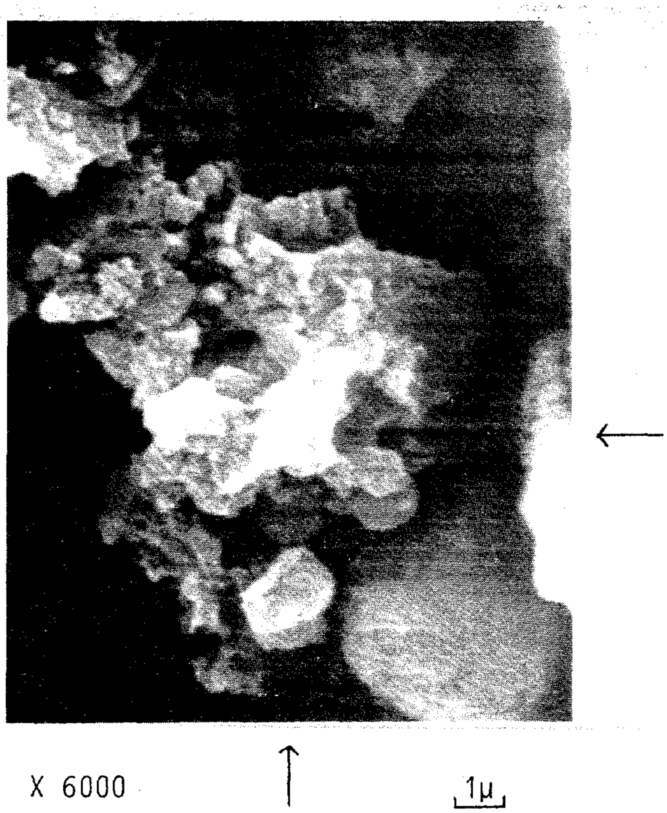
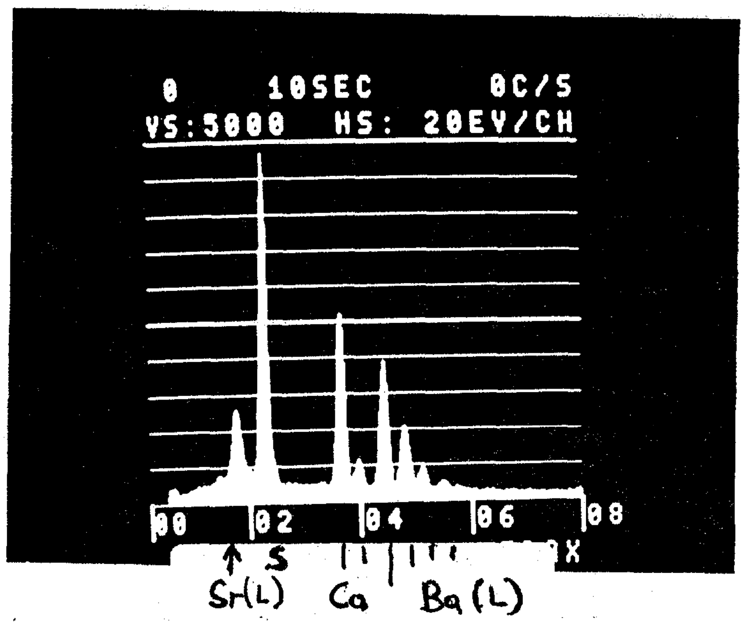


Fig VII Ca, Ba, Sr sulfate
(small crystals deposit)



Radioactive point analysis

Fig VIII

The optimum ratio SRO / BaO is 1/6.

If according to the literature we can extract 20 p.p.m. of Radium per .87 gram of small balls, and if the Radium content of our phosphogypsum is such that we have a 30 pCi/gram α radiation emission, this means that we have $30 \cdot 10^{-12}$ gram of Radium per gram of phosphogypsum, and we will extract $10^{-5}/0.87$ gram of Radium per gram of small balls. In order to extract $30 \cdot 10^{-12}$ gram of Radium, we must produce :

$$30.10^{-12}\,\frac{0.87}{10^{-5}} = 261.10^{-8} \text{ gram of small balls per gram of phosphogypsum.}$$

In order to do this, we need to have :

783.10^{-9} gram of BaO per gram of phosphogypsum, and

130.10^{-9} gram of SrO per gram of phosphogypsum,

that means that we need to have per metric ton of phosphogypsum :

783 mg of BaO

130 mg of SrO.

If there is not enough BaO and SrO in the phosphate, it would be necessary to add BaO and SrO salts into the premix tank in order to get these minimum required amounts.

If we hydrocyclone such a pulp, we can expect to get 95% of usable phosphogypsum in the underflow and 5% of non-usable slurry containing all the Radium, which means $600 \cdot 10^{-12}$ gram of Radium per gram of dry processed phosphogysum.

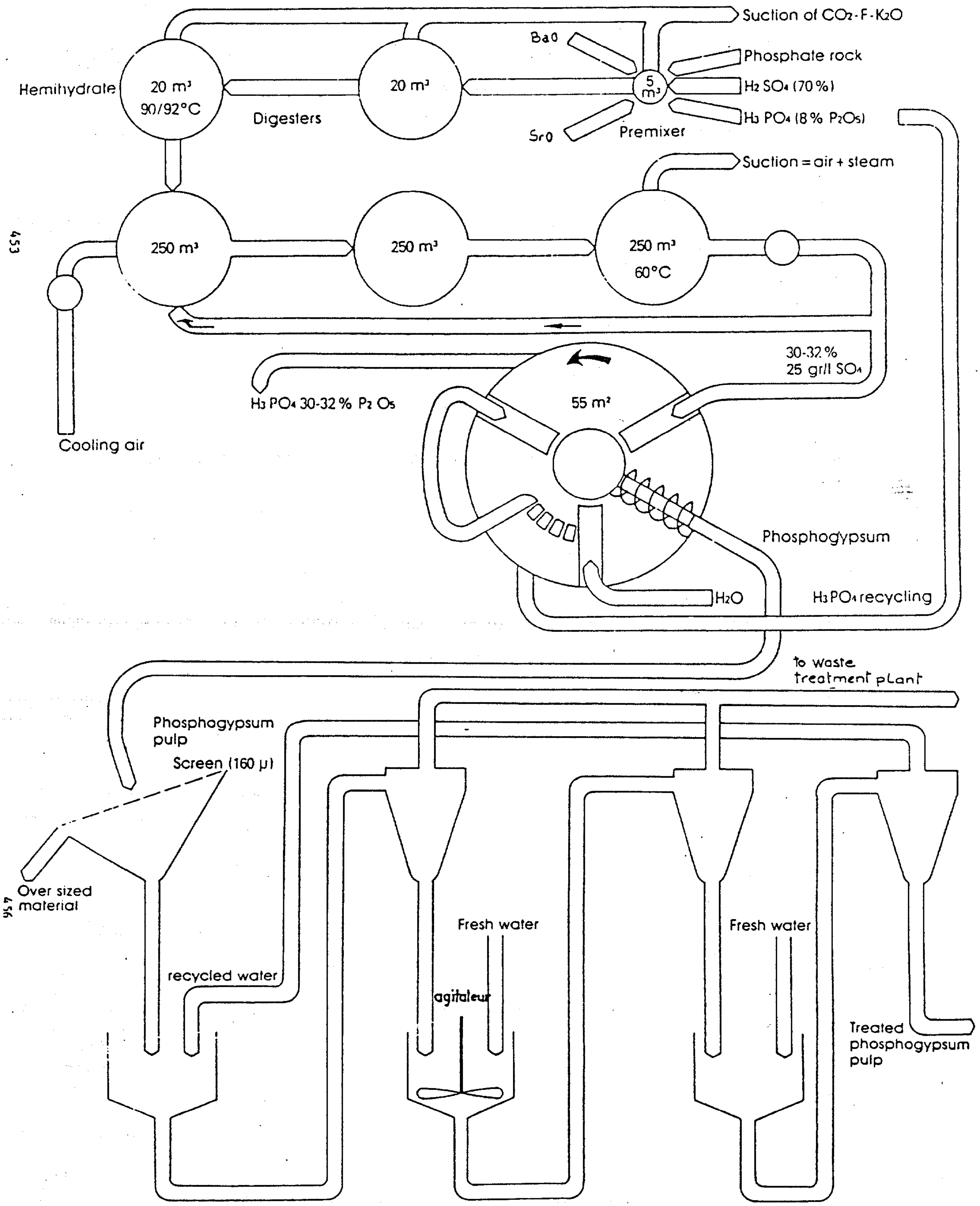
The best ores for use in direct production of phosphogypsum to be treated by the proposed process, or for the repulping of existing phosphogypsum are :

- Barium bromide, Barium acetate, Barium chlorate, Barium chloride, Barium hydroxide, Barium nitrate, and Barium oxide.
- Strontium acetate, Strontium chloride, Strontium hydroxide, and Strontium nitrate.

The same process can be used if stockpiled phosphogypsum is repulped in the premixer of an installation similar to a phosphoric acid plant, by adding the necessary Barium and Strontium (by means of soluble ore containing Barium and Strontium) to digesters at high temperature (90°C). The pulp should be pumped to cooled tanks (60°) in which purified phosphogypsum and co-crystallized Calcium-Strontium-Barium sulfate containin Radium will precipitate. This pulp will have to be filtered, repulped in fresh water and hydrocycloned.

A plant able to achieve our aim could be designed as shown on Fig IX (modified process).

modified Process



fig;9

CONCLUSION

The main problem left is the disposal or treatment of the produced waste with a 600 pCi a radiation emission per gram of product.

It is possible to extract the Radium entrapped in co-crystallized Calcium-Barium-Strontium sulfate by attack of chromic acid or of hydrochloric acid according to a method used by B. GOLDSCHMIDT.

Other similar methods were used by Marie CURIE, O. HAHN, V. KHLOPINE when they tried to extract Radium, without knowing how dangerous Radium was.

This type of extraction is feasible, but what can be done with the extracted Radium at a rate of 30 mgram of Radium for 1,000 T. of purified, phosphogypsum ? If there is an answer to this question, one can envisage industrialization of such a process.

ACKNOWLEDGEMENTS

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We also thank T. WILLIAMSON Vice-President of Research Development of GOLD BOND BUILDING PRODUCTS a Division of NATIONAL GYPSUM who accepted to present this paper at the Second International Symposium on Phosphogypsum.

REFERENCES

- PASCAL - vol. IV - pages 943 - 944 - 945
- B. GOLDSCHMIDT - Annales de la Chimie - page 1388 a 1940.

MASS AND HEAT BALANCES OF A CLEAN TECHNOLOGY PHOSPHORIC ACID PROCESS

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ABSTRACT

Phosphoric acid is mainly used for fertiliser applications. To minimize environmental pollution a new process is being designed. In this process the digestion and the crystallisation stages, which normally occur simultaneously are separated, thus enabling the removal of cadmium ions in between. The aim of this new Clean Technology Phosphoric Acid (CTPA) process is the production of commercially competitive concentrated phosphoric acid (40 w% P_2O_5) with a low cadmium and fluoride content as well as the production of calcium sulphate hemihydrate (HH) with a low cadmium, phosphate and radium content.

This study covers the mass and heat balances of the process. It is the first step towards the engineering flow diagram of a production plant, which can be used to compare this process with existing processes.

First a description of the process stages is given. Thereafter the mass and heat balances for each stage are obtained from the overall mass and heat balances of a 1000 tons P_2O_5 per day producing plant operating according to the CTPA process. These overall mass and heat balances are calculated with the flowsheeting package TISFLO-2. The overall phosphate efficiency of this process is calculated to be about 99%, if wash losses are neglected. Furthermore no external heat seems to be necessary to produce 40 w% P_2O_5 with less than 5 ppm Cd and HH and DH with less than 1 ppm Cd and less than 6.3 w% P_2O_5 incorporated in the crystals. A preliminary study of the investment cost needed for the CTPA process showed hardly any difference with those-needed for a single filter HH/DH (Nissan H) process with the same production capacity.

INTRODUCTION

Phosphoric acid, used for the manufacturing of fertilisers is mainly produced by digestion of phosphate ore with sulphuric acid, the so-called “wet-process". The production of phosphoric acid is expected to rise from about 20 million tons P_2O_5 in 1982 to about 28 million tons in 1990 [Sluis e.a.,1986].

In all wet processes, impurities such as cadmium, radium and fluoride ions, originating from the phosphate ore ($Ca_{10}(PO_4)_6F_2$ + a few w% $CaCO_3$ and quartz), are distributed between the phosphoric acid 2and the by product, a calcium sulphate modification. The use of the byproduct is limited by its phosphate, radium and fluoride content, while the disposal is hampered by its cadmium content [Becker,1983]. The phosphate reduces the strength of the byproduct, while the fluoride reduces its hardening time [Sluis e.a., 1986]. Fluorides can enter the atmosphere via the production process too. They are regarded as serious pollutants [Sluis e.a.,1986]. The decay of radium yields the radioactive radon gas. The most problematic contaminant is, however, cadmium. It is very toxic and can enter the food chain, both via the byproduct and the phosphoric acid. Too high cadmium contents might even prohibit the use of phosphate fertilisers in the future.

In most processes the digestion of phosphate ore and the crystallisation of $CaSO_4.2H_2O$ (DH) or $CaSO_4.\frac{1}{2}H_2O$ (HH) take place more or less simultaneously in the same reactors. [Becker,1983]. The easiest way to remove cadmium therefore seems to be from the ore, before it is introduced in the process. One method to achieve this purpose is calcination of the ore at about 700 °C, the cadmium then evades as CdO. This process, however, requires about 20 MW for a 1000 tons P_2O_5 per day producing plant. Moreover, the solubility of phosphate ore is reduced by calcination, while the fluoride and radium ions remain in the ore. Another method is selective leaching of cadmium from the carbonate fraction of the phosphate ore, which sometimes contains up to 50 w% of the cadmium, by means of digestion of the carbonate containing part of the ore with diluted sulphuric acid with high chloride content [Frankenfield, 1985, Spijker and Hovenkamp,1985]. The chloride ions keep the cadmium as cadmium-chloride complexes in the solution and thus prevent the precipitation of cadmium either as cadmium sulphate or phosphate. Incorporation of cadmium in the calcium sulphate modification produced can therefore also be reduced by feeding complexing agents, such as halogenides to the process liquid. These methods, however, only appear to be satisfactory if the cadmium content of the ore is not too high. Furthermore the cadmium still has to be removed from the phosphoric acid or the leaching solution. In all cases the radium remains in the "phosphogypsum".

A completely different method is based on the separation of the digestion and the crystallisation stages, in order to remove the cadmium ions in between. In this process the possibility is created to optimise the digestion and crystallisation stages independently from each other. Moreover, the radium can be removed before the majority of the calcium ions from the phosphate ore are precipitated as HH. A disadvantage, however, is the large recycle stream of phosphoric acid needed for complete digestion of the phosphate ore.

The aim of this new process, referred to as a Clean Technology Phosphoric Acid (CTPA) process is the production of commercially competitive concentrated phosphoric acid (40 w% P 0) with a low cadmium and fluoride content as well as the production of calcium sulphate hemihydrate (HH) with a low cadmium, phosphate and radium content.

This study considers 'the mass and heat balance of the process. It is the first step towards the engineering flow diagram of a production plant, which can be used to compare this process with existing processes.

PROCESS DESCRIPTION

GENERAL APPROACH

To meet the foregoing requirements the digestion of the phosphate ore and the crystallisation of the HH are separated in two almost independent stages. A simplified flowsheet of the process is shown in figure 1.

First the digestion of phosphate ore proceeds in recycled phosphoric acid. This acid contains sulphate ions in a concentration dictated by the operating conditions in the crystalliser. Part of the calcium ions from the ore will therefore precipitate as HH. Since more than 2 w% P_2O_5 is incorporated in this HH, it cannot be disposed, without lowering the overall phosphate efficiency of the process too much. This HH is thus recrystallised into DH to reduce the phosphate content of the crystals to an acceptable low level (< 0.5 w% P_2O_5).

Before the cadmium ions can be removed, the precipitated HH from the digestion stage, together with the insoluble residue of the ore, have to be separated from the slurry to avoid problems in the cadmium removal stage.

The cadmium can be removed from the almost clear calcium-di-hydrogen-phosphate (CDHP) solution by anion exchange of cadmium halogenide complexes formed by addition of either bromide or iodide ions [Tjioe e.a.,1986].

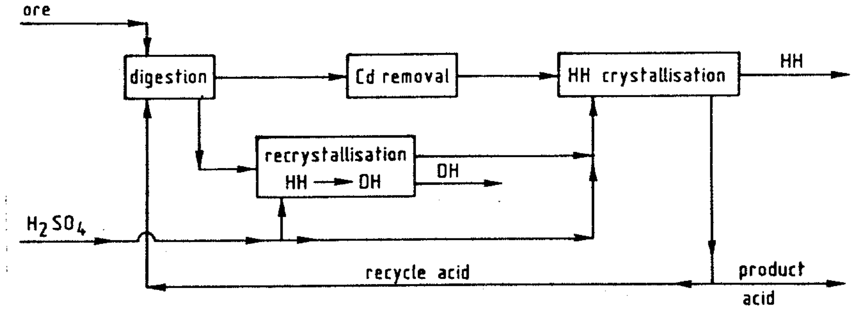

Figure 1: Simplified process flowsheet.

The CDHP solution with a strongly reduced cadmium content is then fed to the crystalliser, together with the recrystallisation liquid and concentrated sulphuric acid. In this crystalliser the calcium ions from the CDHP solution are precipitated as HH. Thereafter the HH is separated by filtration, yielding concentrated phosphoric acid. About 90 w% of this phosphoric acid is recycled to the digestion stage.

The product acid is fed to the iodide or bromide removal stage and finally to the fluoride removal stage. After the removal of the iodide or bromide and the reduction of the fluoride level, concentrated phosphoric acid (40 w% P_2O_5) with a low cadmium and fluoride content is obtained.

DIGESTION OF PHOSPHATE ORE

The digestion stage is proposed to consist of three equally sized stirred tanks in series. The phosphate ore is introduced in the first tank, together with the recycled phosphoric acid and some clay. The clay is used to stimulate the evasion of fluoride. It is the easiest way to add it here, because it can be mixed with the phosphate ore in advance. The quantity of clay (45 w% SiO_2 and 38 w% Al_2O_3) is determined by the additional amount of active silica needed, above the amount already present in the ore, to obtain a molar F/Si ratio of six in the acid.

The composition of the phophate ore used (40 w% Khouribga, 60 w% Zin) is given in table 1.

The phosphoric acid must have a concentration of at least 40 w% P2O5 for direct use in the production of mono- or di-ammonium-phosphate (MAP or DAP) [Becker,1983]. The temperature in the digestion is limited to 95 °C to avoid formation of $CaSO_4.0H_2O$ (AH).

The main reaction occuring under these conditions is:

$$Ca_{10}(PO_4)_6F_2 + 14\ H_3PO_4 \ \text{--->}\ 10\ Ca(H_2PO_4)_2 + 2\ HF$$

Fluoroapatite CDHP

The rate of the digestion is found to be determined by diffusion of calcium ions from the surface of the ore into the bulk of the solution. The maximum solubility of CDHP in phosphoric acid can be expressed as 5.5 w% CaO in 40 w% P_2O_5 at about 95 °C [Becker,1983]. To maintain a safety margin 90 °C, 40 w% P_2O_5 and only 5 w% CaO were chosen as the operating conditions.

The amount of recycled acid needed, is determined by the w% CaO in the CDHP solution after the digestion stage and the sulphate content of the recycled phosphoric acid. For a sulphate content of the recycle stream below 2 w% H_2SO_4, as required to avoid blinding of the ore particles, more than 99 w% of the soluble part of the ore (maximum particle diameter 2 mm) is digested within 90 minutes.

Table 1: Composition of the phosphate ore (Khouribga/Zin 40/60 w%).

component	concentration	component	concentration
moisture	1 w%	Cd	21 mg/kg
CaO	50.8 w%	Cl	380 mg/kg
P_2O_5	31.55 w%	Na	0.56 w%
SO_4	2.4 w%	K_2O	0.08 w%
F	4.2 w%	SiO_2 (total)	1.35 w%
Al_2O_3	0.36 w%	SiO_2 (active)	0.35 w%
Fe_2O_3	0.17 w%	Hg	5 µg/kg
MgO	0.33 w%	Pb	2 mg/kg
CO_2	5.9 w%	Organic C	0.3 w%

The carbonate present in the ore evades as carbon dioxide, saturated with fluoride and water vapour. Due to the presence of organic carbon in the ore, the evasion of carbon dioxide causes excessive foaming. The fluoride in the gas phase is a mixture of hydrogen fluoride and silicon-tetra-fluoride with a mean molar F/Si ratio of six.

The precipitated HH contains cocrystallised P_2O_5, Al, Cd and fluoride. These species are assumed to be incorporated as $CaHPO_4.½H_2O$, $CaAlF_5.½H_2O$ and cadmium ions.

It is furthermore assumed that 50 w% of the fluoride originating from the ore is either cocrystallised with the HH or precipitated. as sodium-fluorosilicate (Na_2SiF_6). Although this fluorosilicate precipitate will partly be deposited as scale, it is assumed, that it leaves the digestion stage with the HH and the insoluble residue of the phosphate ore, which is mainly quartz. These solids are separated from the CDHP solution by a gravity settler, followed by a. decanter centrifuge. Because of the low permeability of the cake obtained after pressure filtration of this slurry, filtration is not a realistic option.

The almost clear CDHP solution is introduced in the cadmium removal stage, while the slurry, containing 50 w% of solids, is fed to the recrystallization stage.

The heat of digestion of the phosphate ore, the heat of crystallization of HH, the heat losses through the vessel walls and the energy dissipation of the turbine stirrers all contribute to the overall heat balance of the digestion stage. The enthalpies of the incoming and outgoing streams are calculated relative to their values at 0 °C with the specific heats given in the appendices. The heat of evaporation of water is taken into account in the enthalpy of the water vapour stream.

CADMIUM REMOVAL

The cadmium removal is assumed to be done in a tubular co-current adsorption. The feed consists of the CDHP solution, a slurry of the strongly basic anion exchange resin in a CDHP solution and iodide ions as complexing agents for cadmium. After passing the adsorber, the anion exchange resin is separated from the solution and almost completely recycled to the entrance of the adsorber. Part of the anion exchange resin is regenerated with water.

The excess iodide is circulating through the whole process and is removed from the product acid, by passing this acid through packed columns of a weakly basic anion exchange resin. This last anion exchange resin is regenerated with concentrated ammonia, after washing of the resin with water to remove the phosphoric acid.

To prevent oxidation of iodide during its passage through the whole process, an adapted amount of iron is added in the digestion stage.

The cadmium and iodide removal stages as well as the amount of iron needed, to prevent oxidation of iodide will be reported elsewhere [Tjioe, 1987]. These stages are not yet included in the mass and heat balances in detail. They can be treated, however, as black boxes, with very little exchange of mass and heat.

Only the amount of water needed for the regeneration of the strongly basic anion exchange resin and for the washing of the weakly basic anion exchange resin is roughly estimated. This water comes from the fluoride removal stage and will be used in the second step of the HH filter cake washing stage, after removal of cadmium from this stream, by either electrolysis or precipitation as a sulphide.

CRYSTALLISATION OF CALCIUM SULPHATE HEMIHYDRATE (HH)

The main reaction in this stage is:

$$2\ Ca(H_2PO_4)_2 + 2\ H_2SO_4 + H_2O \ \text{--->}\ 2\ CaSO_4.\tfrac{1}{2}H_2O + 4\ H_3PO_4$$

This reaction requires a single stirred tank in which the CDHP solution, the concentrated sulphuric acid and the liquid from the recrystallization stage are introduced simultaneously.

To obtain HH crystals with a good filterability the sulphuric acid concentration in the crystallizer must be kept constant at about 1.7 w% H_2SO_4, while a residence time of about 30 minutes is recommended [Sluis e.a., 1986].

The precipitated HH contains cocrystallised P_2O_5, Al, Cd and fluoride in an amount which can be calculated form the correlations and data given in the appendices for all these ions.

The most important heat effect in this stage is the heat of crystallization of HH. The heat of mixing of the acids is quite low, because the major part of the sulphuric acid is almost directly precipitated as HH. The temperature in the crystallizer is maintained at about 90 °C, to prevent formation of AH. The excess heat is removed by evaporation of water in a vacuum slurry cooler. The enthalpies of the streams are calculated, relative to their values at 0 °C, with the heat capacities, given in the appendices.

RECRYSTALLISATION OF HH INTO GYPSUM

The HH formed during digestion of the ore is recrystallized into DH under conditions, similar to those prevailing in commercially known HH to DH recrystallization processes, i.e. at about 60 °C in a solution containing 27 - 30 w% P_2O_5 and about 5 w% H_2SO_4.

The recrystallisation stage is assumed to consist of three equally sized stirred tanks in series. The slurry from the digestion stage, containing about 50 w% CDHP solution, is fed to the first tank, together with the wash water from the HH and the DH filters, concentrated sulphuric acid and half of the DH slurry stream from the third recrystallizer. This slurry stream is recycled to supply enough DH seed material to ensure a high recrystallization rate of HH into DH. A residence time of about five hours should be sufficient for complete conversion of HH into DH [Sluis et.al.,1986].

The produced DH also contains cocrystallised P_2O_5, Cd, Al and fluoride in an amount, which can be obtained from the data and orrelations given in the appendices. The phosphate, Al, and fluoride are assumed to be incorporated as $CaHPO_4.2H_2O$ and $CaAlF_5.2H_2O$ respectively.

The main heat effects are caused by the heat of recrystallisation of HH into DH, the heat of mixing of sulphuric acid with water and phosphoric acid. To maintain a temperature of about 60 °C in the first recrystalliser, water must be evaporated by vacuum slurry cooling. The enthalpies of the streams are calculated, relative to their values at 0 °C, with the heat capacities given in the appendices.

SOLID-LIQUID SEPARATIONS

A belt filter is used for the filtration of both the HH slurry and the DH slurry. The HH as well as the DH crystals are washed three times in counterflow with water. The wash water temperature for the HH washing must be at least 60 °C to avoid recrystallisation into DH on the filter. This would reduce the permeability of the filter cake. The wash water of the DH crystals is assumed to be about 15 °C. The HH as well as the DH crystal cake contain aproximately 30 w% liquid. Neither HH nor DH is assumed to dissolve in the wash water. The HH and DH crystal cake contain 30 w% pure water after the third wash step. This implies negligible P_2O_5 losses due to washing. A small amount of water evaporates during filtration of the DH and HH slurry.

The total amount of water, which can be used as wash water in this process is not only determined by the required concentration of the product acid (40 w% P_2O_5) and the sulphuric acid concentration, but also by the amount of water needed for the regeneration and washing of the anion exchange resins. The washing procedures of the HH and DH cakes are assumed to proceed isothermal.

FLUORIDE REMOVAL

After the iodide removal, the fluoride level in the product acid is reduced to about 0.5 w% F in a packed stripping column. Stripping is achieved with a mixture of carbon dioxide and water vapour of about 90 °C. The stripping gas is, together with the off gasses from the digestion stage, fed to a crossflow scrubber, in which part of the fluoride is removed from the gas mixture through countercurrent washing with water. A 25 w% H_2SiF_6 solution is produced in this scrubber. The largest part of the gas mixture is recycled to the stripping column. The residual gas mixture is disposed, after passing a second scrubber to meet environmental requirements.

The water, to be applied for the HH cake washing, is used in the second scrubber as a scrubbing medium. This scrubber operates at room temperature. The temperature of this wash water is further raised by using it in the direct contact condensor, in which the water vapour from the recrystallisation stage is condensed. Thereafter the temperature is raised to about 60 °C, by applying this wash water for direct contact condensation of the water vapour from the crystalliser.

Since the heat capacities of the streams in the fluoride removal stage are not well known, only a rough estimation of this stage is included in the mass and heat balances.

COMBINED MASS AND HEAT BALANCE FOR EACH STAGE

The balance equations needed to calculate the overall mass and heat balances of the complete CTPA process are for each stage:

- the overall mass balance
- the mass balances for the four components CaO, SO_3, P_2O_5 and water
- the overall heat balance

The fixed operating conditions were:

- 40 w% P_2O_5 in the product acid
- 5 w% CaO in the CDHP solution

- 1.7 w% H_2SO_4 in the crystalliser
- 5 w% H_2SO_4 in the recrystallisers

If the incoming and outgoing streams of a process stage are known, the overall balance equations of each stage can be written.
The mass balances for the components CaO and SO_3 for each stage, can only be applied to solve the overall mass and heat balances of the CTPA process, if the solubility products of HH and DH (appendices) and the compositions of HH and DH are given.

The P_2O_5 mass balance of each stage can be used to solve the total mass and heat balances, if accurate data on the incorporation of phosphate in the HH and DH are known. These data were either measured (see chapter 5) or obtained from literature and are given in appendices.

The composition of the sulphuric acid as well as of the filter cakes and accurate data on the vapour pressure of water above the process streams are needed to be able to use the water balance of each stage. These vapour pressure data are obtained from literature and given in appendices.

The heat balance of each stage requires the enthalpies of reaction, which are given in appendices, and the heat capacities or heat contents of the process streams, which are given in appendices. Information about the heats of mixing of the acids with each other and with water are also needed and are therefore given in appendices.

For the less important components, from the viewpoint of process control, distribution coefficients are used, which for cadmium, aluminum and fluoride are given in appendices.

The complete set of mass and heat balance equations can be solved simultaneously with the software of the flowsheeting simulation package TISFLO-2, developed by DSM. The number of equations must of course be equal to the number of unknown parameters. In this way the overall mass and heat balances of the complete CTPA process can be obtained as well as the composition of the process streams as shown in appendices. From the results given in appendices a mass and a heat balance of each stage can be deduced.

In the following part of this section the overall mass and heat balances of each stage are given and discussed. First of all the digestion stage will be dealt with. The incoming and outgoing process streams of the digestion stage are given in figure 2. In this figure the most important process conditions are given also.

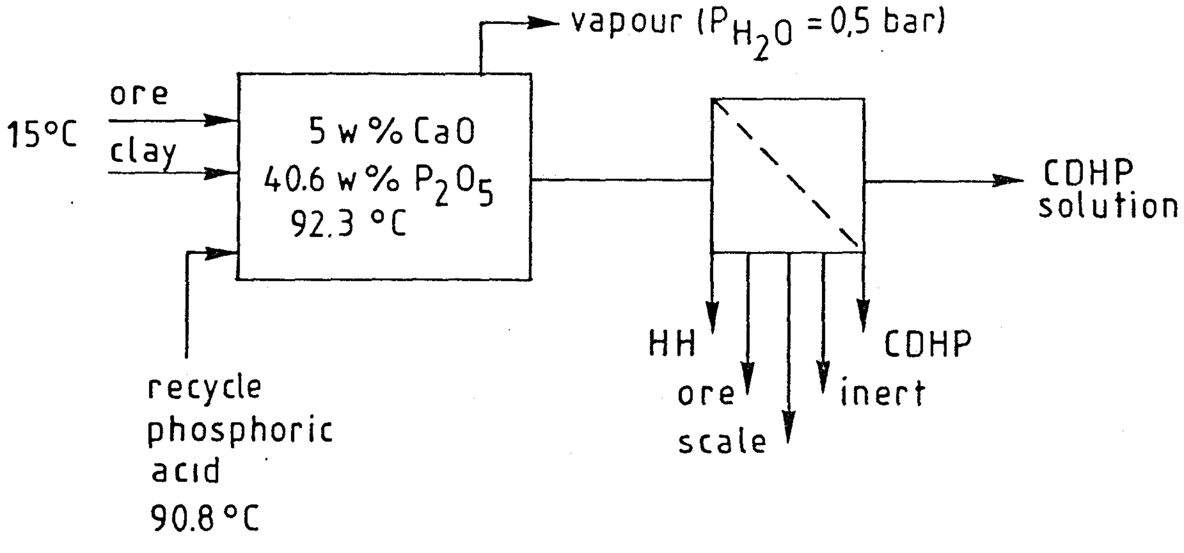

Figure 2: The digestion stage.

The mass and heat balances of this stage are given in table 2a and 2b respectivily.

It is important to notice that the solids content of the slurry, to be fed to the recrystallisation stage, is a critical parameter in this stage. The phosphate concentration in the recrystallisers will raise above 30 w% P_2O_5, if the solid content of this slurry is less than 50 w%. This leads to a reduced conversion rate of HH into DH. As a consequence the recrystallisation of HH into DH will not be completed before the filtration. This can cause a considerable reduction in the overall phosphate efficiency of the whole CTPA process.

Table 2a: Mass balance of the digestion stage (mass streams in kg/s).

component in		component out	
ore	36.7	vapour	3.1
inert	0.4	CDHP solution	300.9
clay	0.8	HH	10.1
recycle acid	288.0	inert	0.4
		ore	0.3
		scale	0.2
		CDHP	10.9
total	325.9	total	325.9

The heat of digestion of the phosphate ore is the second parameter, which has to be discussed. The temperature in this stage can be higher in reality, because the heat of digestion is not accurately known. A twice as high value as used now will raise the temperature of the CDHP solution, however, at most 2 °C, due to the large heat content of the recycle acid stream.

Table 2b: Heat balance of the digestion stage (enthalpies in MW).

component in		component out	
ore, inert and clay	0.4	vapour	2.8
recycle acid	67.2	CDHP solution	66.7
heat of digestion	3.6	HH, inert, ore and scale	0.9
heat of crystallisation	2.0	CDHP	2.4
		heat losses	0.4
total	73.2	total	73.2

After the digestion stage, the almost clear CDHP solution is fed to the cadmium removal stage, which will be reported elsewhere [Tjioe, 1987], as was already mentioned. This stage is regarded as a black box with very little exchange of mass and heat. The most important incoming and outgoing streams are shown in figure 3, while an estimation of the mass and heat balances is given in table 3a and 3b respectively.

The water needed for the regeneration of the strongly basic anion exchange resin and the washing of the weakly basic anion exchange resin, was roughly estimated to be about 2.5 kg per 300 kg of CDHP solution. This number is given only, to be able to deal with the complete process. The amount of water needed is not yet known accurately.

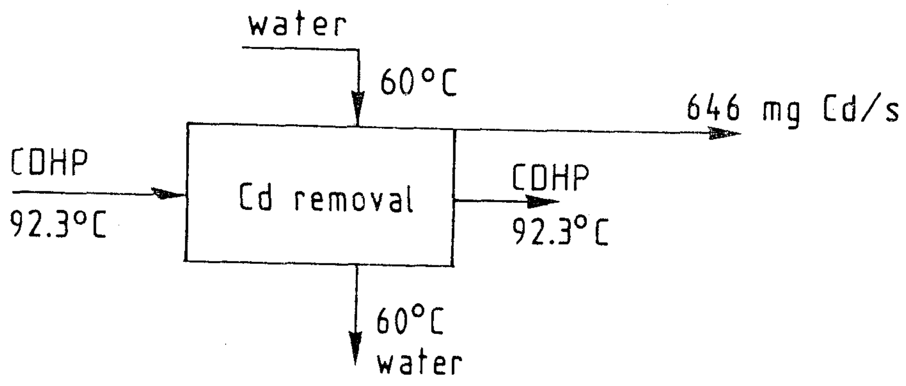

Figure 3: The cadmium removal stage.

Table 3a: Mass balance of the cadmium removal stage (mass streams in kg/s).

component in		component out	
CDHP solution	300.9	CDHP solution	300.6
water	2.5	water	2.8
total	303.4	total	303.4

The water needed for the regeneration and washing of the resins is part of the wash water for the HH filter cake. After its use, the cadmium is removed from the water by electrolysis or by precipitation as a sulphide. Thereafter it is introduced into the process again in the second wash step of the HH filer cake washing stage, because it will contain an appreciable amount of phosphate.

Table 3b: Heat balance of the cadmium removal stage (enthalpies in MW).

component in		component out	
CDHP solution	66.7	CDHP solution	66.7
water	0.6	water	0.6
total	67.3	total	67.3

After the cadmium removal stage, the CDHP solution is introduced into the crystalliser, together with the solution from the recrystalliser and the concentrated sulphuric acid. Figure 4 shows the incoming and outgoing process streams of the crystalliser and the most important operating conditions. The mass and heat balances are given in the tables 4a and 4b.

The most important process parameter in this stage is the sulphate content of the solution in the crystalliser, because this parameter determines the permeability of the HH cake, obtained after filtration of the slurry.

The temperature of the CDHP solution, together with the heat of crystallisation of HH mainly determines the temperature in the crystalliser, which should not exceed about 92 °C, to avoid AH formation.

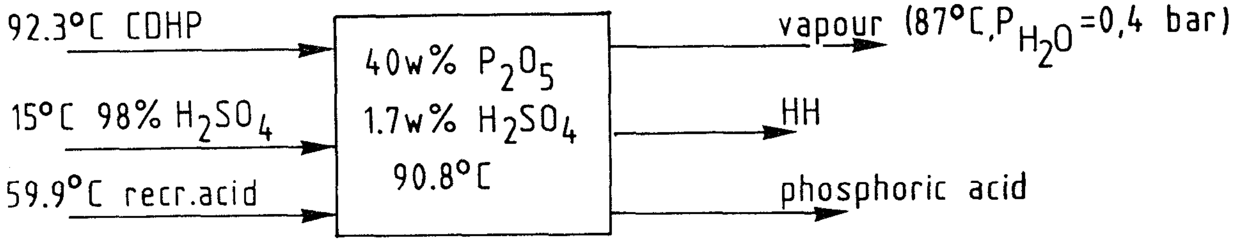

Figure 4: The crystallisation stage.

The excess heat can be removed by evaporation of water in a vacuum slurry cooler. As was already mentioned, the heat of digestion can be higher than the value used in this mass and heat balance. As a consequence, the temperature of the CDHP solution will be higher and more heat has to be removed in this stage.

Table 4a: Mass balance of the crystallisation stage (mass streams in kg/s).

component in		component out	
CDHP solution	300.6	phosphoric acid	333.0
98 w% H_2SO_4	28.8	vapour	0.4
recrystallisation acid	41.2	HH	37.2
total	370.6	total	370.6

This heat, however, can adequately be used for a further raise of the temperature of the wash water for the HH filter cake. The heat removed here is already used for that purpose. This heating of the wash water will be discussed in the fluoride removal stage.

To avoid local primary nucleation of HH or even of AH at the entrance of the CDHP or the sulphuric acid solution in the crystalliser, the mixing of the contents of the crystalliser has to be thoroughly.

Table 4b: Heat balance of the crystallisation stage (enthalpies in MW).

component in		component out	
CDHP solution	66.7	phosphoric acid	77.8
98 w% H_2SO_4	0.7	vapour	1.0
recrystallisation acid	7.2	HH	2.9
		heat losses	0.3
heat of HH crystallisation	7.5	heat of acid mixing	0.1
total	82.1	total	82.1

The recrystallisation acid, mentioned in the tables 4a and 4b, comes from the recrystalliser, in which the HH from the digestion stage is recrystallised into DH.

The incoming and outgoing process streams of the recrystallisation stage are shown in figure 5. The mass and heat balances of this stage are given in the tables 5a and 5b.

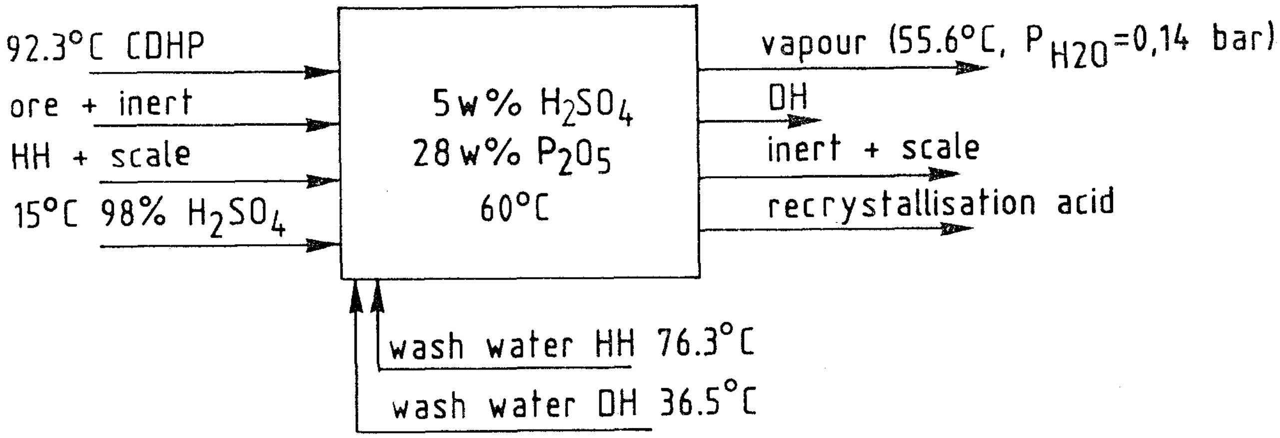

Figure 5: The recrystallisation stage.

In this stage there are two important parameters, which have to be controlled. First of all, the solids content of the slurry coming from the digestion stage must remain equal to or must be higher than 50 w%. If the solids content is lower, more CDHP solution will be fed to the recrystallisation stage. This raises the phosphate content of the solution, and therefore reduces the recrystallisation rate of HH into DH and unacceptable phosphate losses can occur.

Table 5a: Mass balance of the recrystallisation stage (mass streams in kg/s).

component in		component out	
CDHP solution	10.9	recrystallisation acid	47.5
98 w% H_2SO_4	3.7	vapour	0.4
wash water HH	27.6	DH	14.0
wash water DH	10.3	inert	0.4
HH, ore, scale inert	11.0	scale	0.2
total	63.5	total	63.5

In this mass and heat balances, it is already necessary to feed the wash water of the DH as well as of the HH filter cake to the first recrystalliser, to obtain a phosphate content in the recrystalliser, which is low enough to allow recrystallisation of HH into DH in a reasonable time. A recycle stream of 50 w% of the DH slurry from the third recrystalliser, is fed again into the first recrystalliser to achieve a fast conversion of HH into DH.

The second parameter is the heat removal, which is necessary to limit the temperature in the recrystallissation stage to a maximum of about 60 °C. Unless the phosphate content in the recrystallisation stage is chosen to be much lower than 30 w% P_2O_5, the temperature should not be higher, because then conversion of HH into DH will not take place, as follows from the phase diagram of calcium sulphate ([Sluis,1987], chapter 5, figure 1).

The excess of heat has to be removed by evaporation of water in a vacuum slurry cooler, because the vapour pressure of water is very low under these conditions. This vapour pressure can be calculated from the correlations given in appendices.

Table 5b shows that the enthalpy of the wash water of the HH filter cake and the enthalpy of the slurry from the digestion stage, mainly determine the temperature in the recrystallisation stage. If the heat of digestion were higher in reality even more heat has to be removed in this stage.

Table 5b: Heat balance of the recrystallisation stage (enthalpies in MW).

component in		component out	
CDHP solution	2.4	recrystallisation acid	8.3
98 w% H_2SO_4	0.1	vapour	3.5
wash water HH	6.4	DH, scale, inert	0.9
wash water DH	1.1	heat losses	0.2
HH, ore, scale inert	0.9		
heat of mixing of acids and water	1.0		
heat of recrystallisation	1.0		
total	12.9	total	12.9

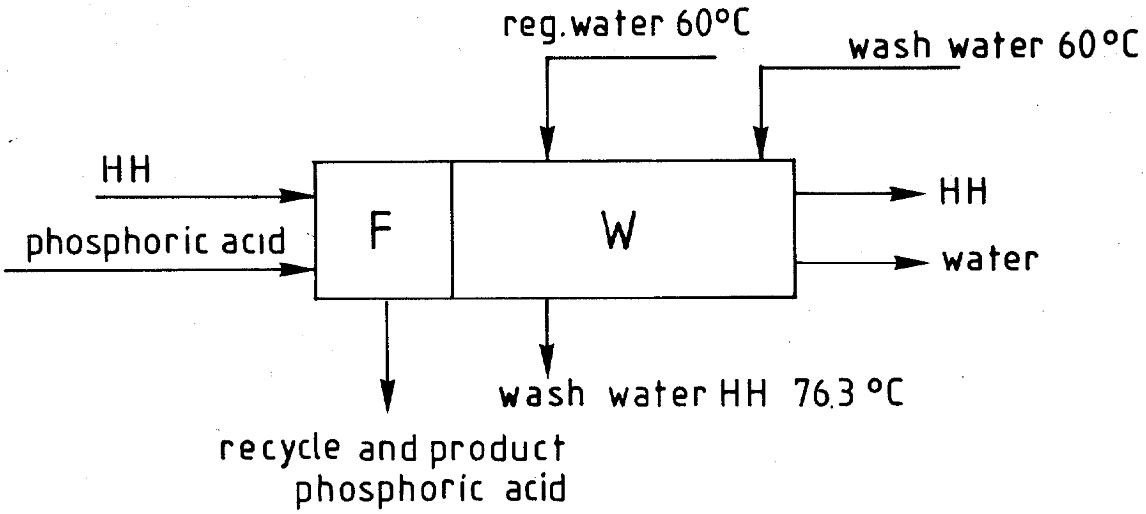

Figure 6: The HH filtration and washing stage.

After the recrystallisation of HH into DH as well as after the crystallisation of HH, the crystal slurries have to be filtered. First the HH filtration and washing stage will be dealt with and thereafter the DH filtration and washing will be discussed. In figure 6 the incoming and outgoing streams of the HH filtration and washing stage are shown. The mass and heat balances are given in the tables 6a and 6b respectively.

Table 6a: Mass balance of the HH filtration and washing stage (mass streams in kg/s).

component in		component out	
phosphoric acid	333.0	phosphoric acid	317.0
HH	37.2	HH	37.2
wash water	24.8	water	16.0
wash water from the cadmium removal stage	2.8	wash water HH	27.6
total	397.8	total	397.8

Table 6b: Heat balance of the HH filtration and washing stage (enthalpies in MW).

component in		component out	
phosphoric acid	77.9	phosphoric acid	74.0
HH	2.9	HH	2.4
wash water	6.2	water	5.2
wash water from the cadmium removal stage	0.6	wash water HH	6.4
heat of mixing of acid and water	0.5		
total	88.0	total	88.0

The heat losses on the filter are neglected. So the temperature of the wash water going to the recrystallisation stage is assumed to be equal to the temperature of the HH leaving the process. If this stage cannot be considered to behave isothermal, the amount of heat to be removed in the recrystallisation stage can change considerably.

The HH leaving the process contains 30 w% water. In practice this water might still contain an amount of phosphate, which cannot be neglected. The liquid content of the HH cake can be influenced by process disturbances. It might be necessary to adjust the amount of wash water used.

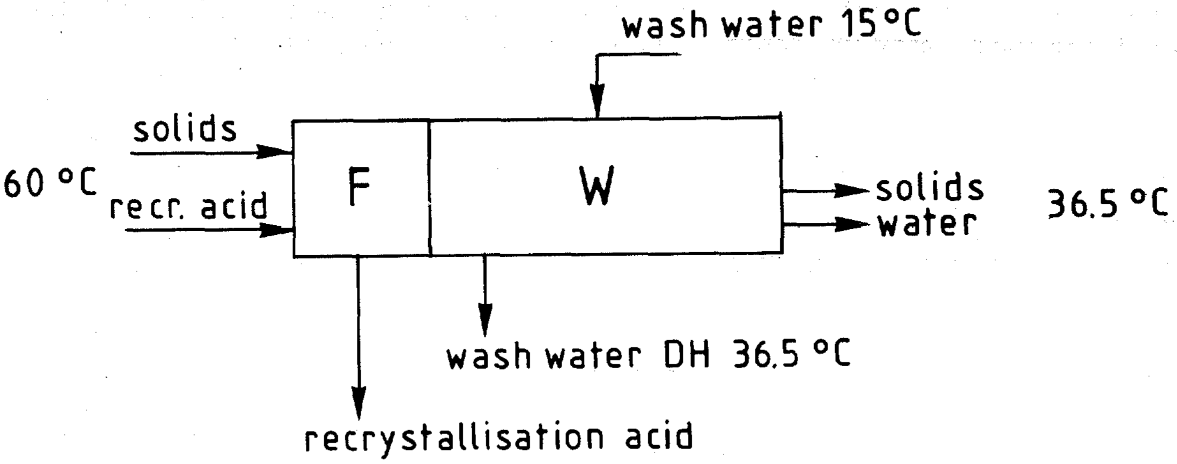

Figure 7: The DH filtration and washing stage.

Table 7a: Mass balance of the DH filtration and washing stage (mass streams in kg/s).

component in		component out	
recrystallisation acid	47.5	recrystallisation acid	41.2
DH, inert, scale	14.6	DH, inert, scale	14.6
wash water	10.3	water	6.3
		wash water DH	10.3
total	72.4	total	72.4

In figure 7 the incoming and outgoing process streams of the DH filtration and washing stage are shown. The mass and heat balances are given in the tables 7a and 7b.

Table 7b: Heat balance of the DH filtration and washing stage (enthalpies in MW).

component in		component out	
recrystallisation acid	8.3	recrystallisation acid	7.2
DH, inert, scale	0.9	DH, inert, scale	0.6
wash water	0.6	water	1.0
heat of mixing of acid and water	0.1	wash water DH	1.1
total	9.9	total	9.9

This stage is also considered to behave isothermal. The phosphate content of the water leaving the process, together with the DH, is neglected too. After washing of the DH filter cake, the wash water is introduced in the first recrystalliser.

The temperature of this wash water is set equal to the temperature of the DH leaving the process. This wash water stream, however, will hardly affect the temperature in the recrystallisation stage.

The last step of the CTPA process is the fluoride removal, This stage is discussed in two parts. The first part deals with the reduction of the fluoride level in the product acid, while in the second part the heating of the wash water of the HH filter cake with the fluoride containing off gasses, is discussed.

Figure 8 shows the incoming and outgoing process streams of the first part, which consists of a stripping column and the first scrubber. The rough values of the mass and heat balances are given in table 8a and 8b.

The stripping column as well as the first scrubber are assumed to operate isothermal. The heat capacity of the fluorosilicic acid solution is set equal to the heat capacity of water and quite rough values for the fluoride distribution coefficient are used. So the data given in table 8a and 8b are only approximations of what will happen in practice.

The stripping gas is mainly carbon dioxide. Before this gas is recycled to the stripping column, the fluoride content of the stipping gas is reduced in the first scribber, which operates at about 90 °C. A part of the stripping gas, as large as the quantity off gasses from the digestion stage, is disposed.

The fluoride content of the gas mixture to be disposed is lowered in a second scrubber, operating at room temperature, to meet environmental requirements.

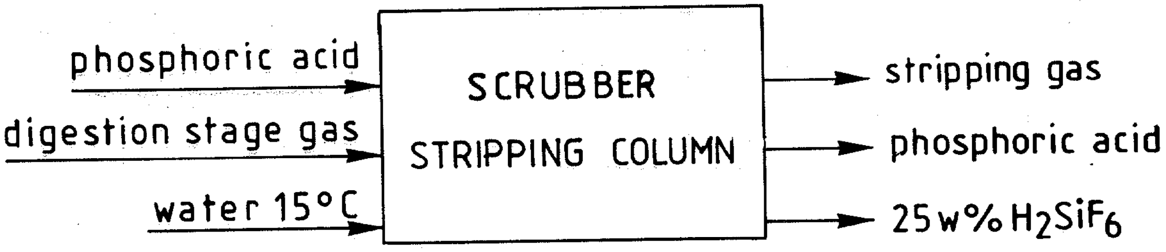

Figure 8: The stripping column and first scrubber

Table 8a: Mass balance of the stripping column and first scrubber (mass streams in kg/s).

component in		component out	
phosphoric acid	28.9	phosphoric acid	28.9
water	3.0	25 w% H_2SiF_6	3.1
off gasses from the digestion stage	3.1	stripping gas	3.0
total	35.0	total	35.0

Table 8b: Heat balance of the stripping column and first scrubber (enthalpies in MW).

component in		component out	
phosphoric acid	6.8	phosphoric acid	6.8
water	0.2	25 w% H_2SiF_6	0.5
off gasses from the digestion stage	2.8	stripping gas	2.5
total	9.8	total	9.8

In figure 9 the incoming and outgoing process streams of the second part of the fluoride removal stage are shown. The mass and heat balances of the second scrubber and the two direct contact condensor are given in the tables 9a and 9b.

Table 9b shows that no external heat is required to raise the temperature of the wash water for the HH filter cake and for the regeneration and washing of the ion exchange resin, to 60 °C. If, however, a higher temperature is required, external heat must be used to raise the temperature unless the heat of digestion of the phosphate ore is much higher than used in these calculations. The calculations for the mass and heat balances of the fluoride removal stage are only roughly, and therefore some external heat might be necessary in practice.

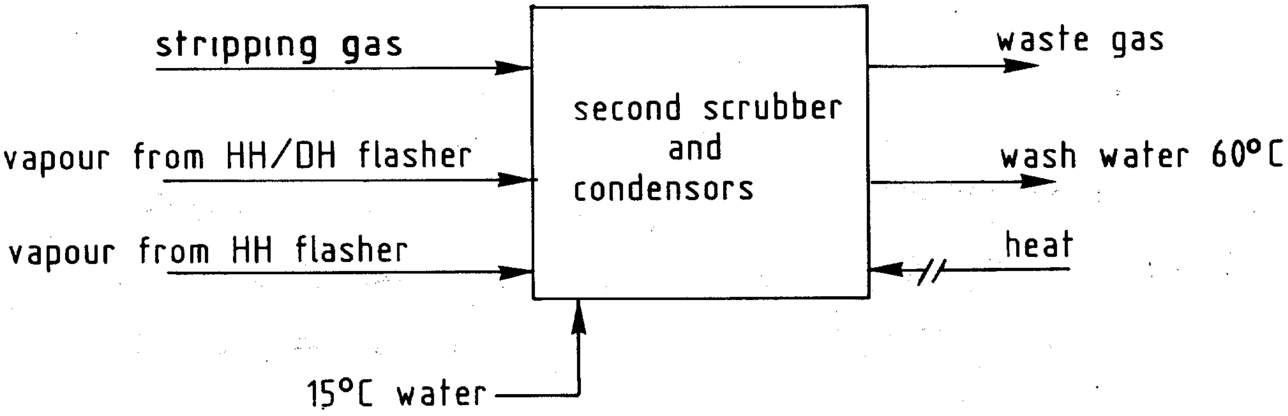

Figure 9: The second scrubber and direct contact condensors.

Table 9a: Mass balance of the second scrubber and direct contact condensors (mass streams in kg/s).

component in		component out	
stripping gas	3.0	waste gas	2.9
water	25.4	wash water	27.3
vapour from the recrystallisation	1.4		
vapour from the crystallisation	0.4		
total	30.2	total	30.2

Table 9b: Heat balance of the second scrubber and direct contact condensors (enthalpies in MW).

component in		component out	
stripping gas	2.5	waste gas	1.8
water	1.6	wash water	6.8
vapour from the recrystallisation	3.5		
vapour from the crystallisation	1.0		
total	8.6	total	8.6

The unwanted deposition of SiO_2 on the walls of the equipment, which is frequently observed in phosphoric acid plants, can have a large influence on the operating efficiency of the scrubbers, of the direct contact condensors as well as of the stripper. It is, however, possible by very adequate temperature control to avoid formation of SiO_2 in the equipment. Therefore, the method proposed for removal of fluoride from the acid and the off gasses should be possible.

DISCUSSION AND CONCLUSIONS

The results given in appendices and presented in the former sections can be put together to give a mass and a heat balance of the complete CTPA process. In table 10 and 11 the mass and heat balances are given of a plant, producing 1000 tons P_2O_5 per day and operating according to the CTPA process. The composition of the products is given in table 12.

The overall phosphate efficiency of the process is calculated to be about 99 % from the amount of phosphate ore used, the amount of phosphoric acid produced and their phosphate content. The phosphate losses, due to incomplete washing of the HH and DH filter cakes are, however, neglected. In practice this assumption will not be fulfilled.

Most of the data and correlations, given in the appendices and used for the calculations, are obtained for chemically pure systems. The influence of impurities is not accurately known, but hardly any influence on the phosphate and cadmium incorporation in the HH crystals is expected ([Sluis,1987], chapter 9).

In practice, the overall phosphate efficiency of the process will therefore, be less than 99 %, but the specification of the products (a maximum cadmium concentration in the phosphoric acid of 5 ppm and in the HH and the DH of 1 ppm) can still be reached.

Table 10: Overall mass balance of the CTPA process (mass streams in kg/s).

component in		component out	
phosphate ore	37.1	phosphoric acid	28.9
clay	0.8	HH-slurry	53.2
water	38.7	DH-slurry	20.9
98 w% H_2SO_4	32.4	25 w% H_2SiF_6	3.1
		waste gas	2.9
total	109.0	total	109.0

Table 11 shows that no external heat is required in the CTPA process. The results obtained so far, show that the production of concentrated and "clean" phosphoric acid and "clean phosphogypsum" should be possible with the CTPA process.

Table 11: Overall heat balance of the CTPA process (enthalpies in MW).

component in		component out	
ore and clay	0.4	phosphoric acid	6.8
98 w% H_2SO_4	0.8	HH-slurry	7.6
water	2.4	DH-slurry	1.6
heat of digestion	3.6	25 w% H_2SiF_6	0.5
heats of mixing	1.5	waste gas	1.8
heats of crystallisation	9.5	heat losses	0.9
heat of recrystallisation	1.0		
total	19.2	total	19.2

Table 12: Composition of the products of the CTPA process.

phosphoric acid	HH	DH
40 w% P_2O_5 1.7 w% H_2SO_4 0.5 w% F^- 4 ppm Cd	0.4 ppm Cd 0.2 w% P_2O_5	0.2 ppm Cd 0.3 w% P_2O_5

Additional information about the heat of digestion, about the cadmium removal stage as well as about the fluoride removal stage is, however, required to make a complete engineering flow diagram of the CTPA process.

A reasonably sized pilot plant, in which all process steps are incorporated is needed to confirm the results given here. Only in a process in which all impurity levels are build up, accurate data for the description of the cadmium as well as of the fluoride removal stage can be obtained.

A preliminary study of the investment needed to build a plant operating according to the CTPA process and to build a plant operating according to a single filter HH/DH process, with the same production capacity, showed hardly any difference in investment cost.

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LITERATURE

Becker, P., Phosphates and Phosphoric Acid, Fertiliser Science and Technology Series, Vol. 3, Marcel Dekker Inc., New York, (1983).

Bos, W.S., Private Communications, Windmill B.V., Vlaardingen, (1985).

Edukos, A.T. and Ikonomu, E., Zh. Prikl. Khim., 58, 9, (1985) 1937.

Egan, E.P.jr. and Luff, B.B., Ind. Eng. Chem., 47 (1955) 1280.

Egan, E.P.jr. and Luff, B.B., J. Chem. Eng. Data, 11 (1966) 509.

Egan, E.P.jr., Luff, B.B. and Wakefield, Z.T., J. Phys. Chem., 62 (1958) 1091.

Elmore, K.L. and Farr, T.D., Ind. Eng. Chem., 32 (1940) 580.

Farr, T.D., Tennesee Valley Authority, Chem. Eng. Report 8 (1950) 44.

Frankenfield, K., Verfahren zur Entfernung von Cadmium aus Phosphaterzen, Chemische Fabrik Budenheim, DE-3332698 A1, 21 maart 1985.

Frochen, J., Laine, J., Allyot, H. and Gosse, G., Concentrated Phosphoric Acid Manufacturing Process by Double Crystallisation, Bulletin d'Information HEURTEY, 57 (1972).

Gaubert, P., C.r., 197 (1933) 72.

Giauque, W.F., Hornung, E.W., Kunzler, J.E. and Rubin, T.R.,
J. Am. Chem. Soc., 82 (1960) 62.

Glazyrina, L.N., Savinkova, E.I. and Grinevich, A.V.,
Zh. Prikl. Khim., 53, 11 (1980) 2524.

Ivanchenko, L.G., Guller, B.D., Zinyuk, R.Yu. and Peresvetova, S.A.,
Issled. V:Obl. Tekhnol. Mineral Udobr., L (1983) 58.

Kelley, K.K., Southard, J.C. and Anderson, T.C.,
Techn. Pap. Bur. Mines; nr. 625 (1941) 1:

Knobeloch, J.B. and Schwartz, C.E., J. Chem. Eng. Data, 7 (1962) 386.

Klocko, M.A. and Kurbanov, M.S.,
Ivzestija Sektora Fiz.-Chim. Anal., 24 (1954) 252.

Laptev, V.M., Kopylov, B.A., Varshavskii, V.L. and Ovsyannikova, L.G.,
Sbornik Trudov/Leningradskii Tekhol. Inst. Im Lensovita, 4 (1973) 11.

Linck, G. and Jung, H., Z. Anorg. Chem., 137 (1924) 407.

Perry, R.H. and Green, D.W., Ed., Perry's Chemical Engineers' Handbook,
6th. ed., McGraw-Hill Book Co., New York, 1984.

Rakshit, J.N., Z. Electrochemie, 32 (1926) 276.

Riddell, W.C., Rock. Prod., 53 (1950) 68, 102.

Rosincky, V. and Kockta, J., Spisy Priradovedeckou Fak. Musarykovy Univ.,
nr. 210 (1935) 3.

Skauge, A., Fuller, N. and Hepler, L.G.,
Thermochimica Acta, 61 (1983) 139;

Slack, A.V., Ed., Phosphoric Acid, Fertiliser Science and Technology Series,
Vol. 1, Marcel Dekker Inc., New York, 1968.

Sluis, S. van der, Meszaros, Y., Wesselingh, J.A. and Rosmalen, G>M> van,
Proc. Fertiliser Society of London, nr. 249; (1986).

Sluis, S. van der, PhD Thesis, Technical University of Delft, Delft, 1987.

Smith, A. and Huffman, E.O.,
Ind; Eng. Chem. Chem. Eng. Data Ser., 1, 1 (1956) 99.

Sokolik, S., Z. Physik. Chem., Al58 (1932) 305.

Spencer, L.J., Mineralog. Mag., 21 (1926/1928) 337.

Spijker, R. and Hovenkamp, H.,
UKF-rapport YBO-ME-85-3974, 12 december 1985.

Taperova, A.A., J. Appl. Chem. USSR., 18 (1945) 521.

Tjioe, T.T., Weij, P. and Rosmalen, G.M. van,
Proc. World Congress 111 Chem. Eng., Tokyo, Japan, Vol 2, (1986) 925.

Tjioe, T.T., PhD Thesis, To be published (1987), Technical University of Delft.

Tutundzic, P.S., Liler, M. and Kosanovic, D.,
Glasnik. Hem. Drustva. Beograd., 20 (1955) 1.

Wakefield, Z.T., Luff, B.B. and Reed, R.B.,
J. Chem. Eng. Data, 17, 4 (1972) 420.

Weast, R.C. and Astle, M.J., Handbook of Chemistry and Physics,
CRC Press, Cleveland, Ohio, 59th. ed. (1979).

Weterings, K., The Development of a Clean Technology Phosphoric Acid
Process, DSM Research B.V., Report of 5 april 1985.

Wulff, P. and Schaller, A., Z. Krist., 87 (1934) 43.

Yudenkova, I.N. and Ishchenko, N.A.,
Zh. Prikl. Khim., 55, 5 (1982) 1162.

Zinyuk, R. Yu., Rogova, G.I. and Pozin, M.E.,
J. Appl. Chem. USSR., 44, 10 (1971) 2316.

APPENDICES

THE SOLUBILITY OF HH AND DH

The solubility product K_{HH} for HH, defined as: K_{HH} = w% CaO * w% SO_4, is calculated from data given in literature [Giauque e.a.,1960,Glazyrina e.a.,1980,Laptev e.a.,1973,Slack,1968,Taperova,1945] as:

$$K_{HH} = 623 * e^{((-1277 + 36 * w\%\ P_2O_5)/T)},$$

where the weight percentages, are those present in solution and T is the absolute temperature.
The solubility product K_{DH} for DH, defined as: w% Ca * (w% $SO_4)^n$, is given by Becker [Becker,1983] as:

$$K_{DH} = 0.460 * \frac{w\%\ P_2O_5}{100} * ((2.40 - \log(T-273))/0.912),$$

in which n = 1.25 - 0.01 * (T-273).
The weight percentages are those in solution and T is the absolute temperature.

INCORPORATION IN HH AND DH

Incorporation in calcium sulphate hemihydrate

The phosphate incorporation in HH can be expressed as [Sluis e.a.,1986]:

$$\frac{w\%\ P_2O_5\ \text{in HH}}{w\%\ SO_3\ \text{in HH}} = 1.4 * 10^{-4} * \frac{w\%\ P_2O_5\ \text{in solution}}{w\%\ SO_3\ \text{in solution}}$$

The cadmium incorporation in HH was estimated by [Sluis e.a.,1986]:

$$\frac{\text{mol Cd per kg HH}}{\text{mol Ca per kg HH}} = 1 * 10^{-3} * \frac{\text{mol Cd per kg solution}}{\text{mol Ca per kg solution}}$$

In the presence of 240 ppm I−, the value of $1 * 10^{-3}$ must be replaced by $5 * 10^{-4}$, because the given iodide content reduces the cadmium incorporation by about a factor two ([Sluis,1987], chapter 5).
Data obtained in the bench-scale plant ([Sluis,1987], chapter 9) revealed that:

$$\frac{\text{w\% Al in HH}}{\text{w\% Al in solution}} = 0.4$$

Since the fluoride in the HH crystals is incorporated as AlF_5^{2-}, which replaces SO_4^{2-} in the HH lattice ([Sluis,1987],chapter 5), the fluoride content of the HH crystals also follows from the former equation.

Incorporation in calcium sulphate dihydrate

According to Frochen e.a. [Frochen e.a.,1972], the phosphate incorporation in DH is given by the equation:

$$\text{w\% } P_2O_5 \text{ in DH} = 0.01 * e^{(-0.0554 - 0.3276 * fsc + 0.0218 * fsc^2)},$$

in which fsc = percentage of free sulphuric acid in the solution.

The free sulphuric acid content of a solution equals the total sulphate concentration in the solution, expressed as mol per kg, minus the calcium concentration in the solution, also expressed as mol per kg.

The cadmium incorporation in the DH is given by:

$$\frac{\text{ppm Cd in HH}}{\text{ppm Cd in solution}} = 0.1,$$

which value has been found in a commercial plant, operating under similar conditions [Weterings,1985]. In the presence of 240 ppm iodide the value of 0.1 must be replaced by 0.05, due to the reduction of the cadmium incorporation by formation of cadmium-iodide complexes.
The incorporation of Al and F is assumed to be the same as for HH.

VAPOUR PRESSURE OF THE P_2O_5-H_2O SYSTEM

The correlations, used for predicting the vapour pressure of phosphoric acid solutions in the CTPA process are based on data measured by Farr [Farr,1950].

$$\log P = -(2935.61 - 0.122287 * n + 0.022738 * n^2)/T - 4.9373 * \log T + 1.6939 * 10^{-5} * T + 4.874 * 10^{-8} * T^2 + 25.5525 - 1.1237 * 10^{-3} * n + 1.1216 * 10^{-5} * n^2$$

for $0 \leq$ w% $P_2O_5 \leq 23.5$ and

$$\log P = -(2944.79 - 1.6128 * n + 0.02113 * n^2)/T - 4.9373 * \log T + 1.6939 * 10^{-5} * T + 4.874 * 10^{-8} * T^2 + 25.4825 - 2.7695 * 10^{-3} * n + 2.3186 * 10^{-5} * n^2$$

for $23.5 \leq$ w% $P_2O_5 \leq 38.2$ and

$$\log P = -(3667.44 - 33.802 * n + 0.42947 * n^2)/T - 4.9373 * \log T + 1.6939 * 10^{-5} * T_2 + 4.874 * 10^{-8} * T^2 + 25.7501 - 5.0125 * 10^{-3} * n + 4.4405 * 10^{-5} * n^2$$

for $38.2 \leq$ w% $P_2O_5 \leq 63.7$,

in which P = water vapour pressure in Pa
T = temperature in K
n = w% P_2O_5 in the solution

These correlations are used for all the streams in the CTPA process. Sulphuric acid or other species, present in the solution, were treated as water.

In the digestion stage, the vapour pressure of water above the phosphoric acid is equal to the partial vapour pressure of water. The absolute pressure of 1 bar is the sum of the partial vapour pressure of water and the vapour pressures of carbon dioxide and the various fluoride compounds.

FLUORIDE DISTRIBUTION COEFFICIENTS

Liquid-gas

If the composition of the solution is known, the concentration of fluoride in the gas phase can be estimated by the equation ([Sluis,1987], chapter 7):

$$\ln H = 32.4 + \frac{2}{3} * \ln(m(H^+)) - \frac{2}{3} * \ln(m(H_2SiF_6)) + 0.156 * m(H_3PO_4) + m(H_2SiF_6) + 0.457 * m(H_2SO_4) - \frac{9550}{T},$$

in which $H = \frac{\text{mg F / m}^3\text{ vapour}}{\text{mol H}_2\text{SiF}_6\text{ / kg H}_2\text{O}}$
m(x) = mol of species x per kg of water in the solution
T = temperature in K

For the digestion, the crystallisation and the fluoride removal stages a value of 10^4 mg F/m^3 vapour/w% F in the solution was used, while a value of 100 mg F/m^3 vapour/w% F in the solution was used for the recrystallisation stage.

Liquid-solid

The total amount of fluoride deposited as Na_2SiF_6, K_2SiF_6 and $NaKSiF_6$, is difficult to estimate, because a supersaturated solution of these compounds can easily be maintained. It was therefore quite arbitrary assumed, that in the CTPA process, half of the fluoride present in the ore, leaves the process as solids, as was also found in a commercial single stage HH process [Bos,1985].
The incorporation of fluoride in the HH and the DH has already been defined. The amount of fluoride precipitating with the HH and DH is less than 50 w% of the fluoride present in the phosphate ore. So the remaining part of the fluoride, to be precipitated, will be deposited as a fluorosilicate precipitate, also called scale. Furthermore, it is assumed that, this scaling will be formed only in the digestion stage, where the fluoride is added and in the recrystallisation stage, where the temperature is lowered from 90 to 60 °C. The fluoride deposited as scale, is assumed to be sodium fluorosilicate only; The fictitious solubility products used in the separate stages are:

$$K(\text{digestion}) = [Na+] * [SiF_6^{2-}] = 1.766 * 10^{-2} \text{ mol}^2/\text{kg}^2$$

$$K(\text{recrystallisation}) = 3.295 * 10^{-3} \text{ mol}^2/\text{ kg}^2$$

The clay, introduced in the digestion stage, was assumed to contain no sodium ions. Other values of the solubility products have to be used, if the clay contains sodium ions. The fluoride deposited as scale as well as the fluoride incorporated in the HH and DH is assumed to leave the process with the HH and DH respectively. In practice the scale will be deposited on the walls of the reactors and cleaning of the reactors is needed frequently.

DENSITY CORRELATIONS

Phosphoric acid

The density of chemically pure phosphoric acid was derived from literature data [Egan and Luff,1955,Klocko and Kurbanov,1954] and fitted between 0 - 95 °C and 0 - 70 w% P_2O_5 with the following correlation:

$$\rho = ((-6.135 * w - 4.2450) * 10^{-4} * (T - 273) + 1.0073 + 0.7487 * w + 0.4258 * w^2 + 0.3237 * w^3) * 10^3$$

in which ρ = density of phosphoric acid in kg/m^3
w = w% P_2O_5 in solution
T temperature in K

Sulphuric acid

The density of sulphuric acid was derived from literature data [Perry and Green, 1984] and fitted between 0 - 100 °C and 0 - 100 w% H_2SO_4 with the following correlation:

$$\rho = e^{(0.83222 * w - 0.00046944 * (T - 273) + 6.9128)} - e^{(-14.9985 + 0.069634 * (T - 273) + (24.484 - 0.086606 * (T - 273)) * w)}$$

in which ρ = density of sulphuric acid in kg/m^3
w = w% SO_3 in solution
T = temperature in K

CDHP solutions

The following correlations were obtained by fitting the literature data [Elmore and Farr,1940,Smith and Huffman,1956] between 0 - 70 w% P_2O_5, 0 - 95 °C and between 0 w% CaO and the saturation concentration of CaO in the solution:

$$\rho(T,w,c) = \rho(T,w) + c * fc * 10^3$$

in which $\rho(T,w,c)$ = density of the CDHP solution, containing w w% P_2O_5, c w% CaO at a temperature of T kelvin.
$\rho(T,w)$ = density of chemically pure phosphoric acid at the given temperature and phosphate content
c = w% CaO
fc = 1.05 + 0.00225 * (T - 273) + 1.9 * w
T = temperature in K

H_3PO_4-H_2SO_4-H_2O mixtures

According to Tutundzic e.a. [Tutundzic e.a.,1955] and Yudenkova and Ishchenko [Yudenkova and Ishchenko,1982], the sum of the fractional contributions of the pure components can be used.

Calcium sulphate hemihydrate (HH)

HH can occur in two different modifications, the so-called α and β forms. The β form is dehydrated gypsum, while the α form develops from solutions. So in the CTPA process the α form of HH is precipitated. The density of the α form is taken to be the mean value of the data given in literature [Gaubert,1933,Kelley e.a.,1941,Linck and Jung,1924,Rosincky and Kockta,1935]:

$\rho = 2746\ kg/m^3$, st. dev. 11 kg/m^3

Calcium sulphate dihydrate (DH)

The mean value of the density, obtained from literature data [Kelley e.a.,1941,Perry and Green,1984,Rakshit,1926,Spencer,1928,Wulff and Schaller,1934] is:

$\rho = 2312\ kg/m^3$, st. dev. 6 kg/m^3

The phosphate ore

The density of the Zin phosphate ore was determined to be approximately 2700 kg/m^3, as measured by the pyknometer method ([Sluis,1987], chapter 4).

Water

From literature data [Weast and Astle,1979] the following expression for the density of water is obtained:

$$\rho = 1006,287 - 0.42876 * (T - 273)$$

in which ρ = density of water in kg/m^3 and T = temperature in K

HEAT CAPACITIES AND HEAT CONTENTS

Phosphoric acid

From literature data [Egan e.a.,1958,Wakefield e.a.,1972] the following correlation was obtained for chemically pure phosphoric acid:

$$cp = (3725.80 + 2.23326 * (T - 273) - 32.5439 * w - 0.00310846 * (T - 273)^2 + 0.0236263 * w^2 + 0.00887146 * (T - 273) * w) * 10^{-3}$$

in which cp = heat capacity in kJ/kg/K, w = w% P_2O_5 in sollution and
T = temperature in K

Sulphuric acid

According to literature data [Sokolik,1932], the heat capacity of chemically pure sulphuric acid is nearly temperature independent and can be approximated with the following correlation:

$$cp = 4.19 * (1 - (9.8177 * 10^{-3} * w - 4.9327 * 10^{-5} * w^2 + 1.5081 * 10^{-7} * w^3))$$

in which cp = heat capaciry in kJ/kg/K
w = w% SO_3 in solution

CDHP solutions

From literature data [Egan and Luff,1966], the following equation was obtained for chemically pure CDHP solutions:

$$cp = (4175.09 - 49.1067 * c - 45.1056 * w + 1.59092 * c * w + 0.0974336 * w^2 - 0.0270606 * c * w^2 + 2 * (T - 298)) * 10^{-3}$$

in which cp = heat capacity in kJ/kg/K, c = w% CaO in solution,
w = w% P_2O_5 in solution and T = temperature in K

H_3PO_4-H_2SO_4-H_2O mixtures

For lack of data on this system, the correlation given above for phosphoric acid was used. The sulphuric acid content of the solution was neglected and considered to be water. After all calculations were performed, a reinvestigation of the data given in literature [Knobeloch and Schwartz,1962], made it possible to derive the following expression for the heat capacity of this mixtures:

$$cp = (x_1 * (18.0726 - 4.4635 * 10^{-3} * T + 6.7299 * 10^{-5} * T^2 - 1.4873 * 10^{-7} * T^3) / 18.0152 + x_2 * (32.07 + 3.923 * 10^{-2} * T) / 98.0774 + x_3 * (0.1568 + 8.748 * 10^{-4} * T - 2.316 * 10^{-7} * T^2)) * (x_3 / 0.2)^{0.05}$$

in which cp = heat capacity in cal/g/°C, T = temperature in °C
x_1 = w% H_2O, x_2 = w% H_2SO_4 and x_3 = w% P_2O_5

The deviations between the experimental values, between 30 -90 °C, and those predicted by the correlation given above is maximal 3 %.

Calcium sulphate hemihydrate (HH)

The heat capacity of the α form of HH is given by [Kelley e.a.,1941,Riddell,1950] and equals:

$$cp = (488.4 + 1.13 * T) * 10^{-3}$$

in which cp = heat capacity in kJ/kg/K and T = temperature in K

Calcium sulphate dihydrate (DH)

According to Riddell [Riddell,1950], the following correlation, based on data of Kelley [Kelley e.a.,1941], can be used to estimate the heat capacity of DH:

$$cp = (530.7 + 1.84 * T) * 10^{-3}$$

in which, cp is given in kJ/kg/K and the temperature in K.

The phosphate ore

According to literature data [Egan e.a.,1958], the following expression can be used to estimate the heat capacity of phosphate ore:

$$cp = (937.6 + 0.1189 * T - 20.25 * 10^6 * T^{-2}) * 10^{-3}$$

in which, cp is given in kJ/kg/K and the temperature in K.

Water

The heat content data, given by Weast and Astle [Weast and Astle,1979], are used to derive the following expression for the heat content of water, relative to 0 °C:

$$H = 4.80296 * 10^{-2} + 4.2003 * (T - 273) - 5.05431 * 10^{-6} * (T - 273)^{2} + 4.10118 * 10^{-6} * (T - 273)^{3}$$

in which H = heat content in kJ/kg and T = temperature in K.

Water vapour

The heat content of water vapour can be calculated from literature data [Perry and Green,1984,Weast and Astle,1979] with the following equation, obtained from TISDATA, the databank for physical parameters of DSM:

$$H = (44864.1 + 36.8545 * (T - 273) - 506.193 * P + 2.88044 * (T - 273) * P - 1.351176 * 10^{-2} * (T - 273)^{2} - 14.1243 * P^{2}) / 18.0153$$

in which H = heat content in kJ/kg, T = temperature in K and
P = vapour pressure of water in bar

Carbon dioxide

From the databank of DSM, TISDATA, the following expression for the heat capacity of carbon dioxide was obtained [Perry and Green,1984]:

$$cp = (21.3548 + 6.425188 * 10^{-2} * T - 4.103002 * 10^{-5} * T^{2}) / 44.01$$

in which cp = heat capacity in kJ/kg/K and T = temperature in K

Other compounds

The contribution of SiF_4 and HF to the heat capacity of the gas streams is neglected, while the heat capacity of the Na_2SiF_6 scale is arbitrary set equal to 0.75 kJ/kg/K. After all calculations were performed, it was found that a value of 1 kJ/kg/K is more realistic [Perry and Green,1984]. The heat capacity of clay is 0.94 kJ/kg/K [Klocko and Kurbanov,1954]. This value is used, because the type of clay to be used is not yet known. If the type of clay to be applied is known, then the heat capacity of the clay, as a function of the temperature, can probably be obtained from the data and correlations given by Skauge e.a. [Skauge e.a.,1983]. The heat capacity of the H_2SiF_6 solution is set equal to the heat capacity of water, because there are no literature data found for this solution.

ENTHALPIES OF REACTION

Digestion of phosphate ore

$$Ca_{10}(PO_4)_6F_2 + 14\ H_3PO_4 \text{--->} 10\ Ca(H_2PO_4)_2 + 2\ HF$$

ΔH ≈ - 100 kJ/kg ore [Edukos and Ikonomu,1985]

Crystallisation of calcium sulphate hemihydrate (HH)

$2\ Ca(H_2PO_4)_2 + 2\ H_2SO_4 + H_2O \longrightarrow 2\ CaSO_4 \cdot \frac{1}{2}H_2O + 4\ H_3PO_4$

ΔH = -200 kJ/kg HH [Zinyuk e.a.,1971]

Recrystallisation of HH into DH

$2\ CaSO_4 \cdot \frac{1}{2}H_2O + 3\ H_2O \longrightarrow 2\ CaSO_4 \cdot 2H_2O$

ΔH = - 100 kJ/kg HH [Riddell,1950]

All values are rough approximations, because they are mainly determined in water and no accurate data are available at the conditions prevailing in the CTPA process. These data, however, will be measured in the near future and for the time being, the values of the heats of reaction, given above are used.

HEAT OF MIXING IN THE H_3PO_4-H_2SO_4-H_2O SYSTEM

General procedure

Knobeloch and Schwartz [Knobeloch and Schwartz,1962], have given a method to calculate the heat of mixing in a ternary system, from the heats of mixing in the three binary systems (see figure 1).

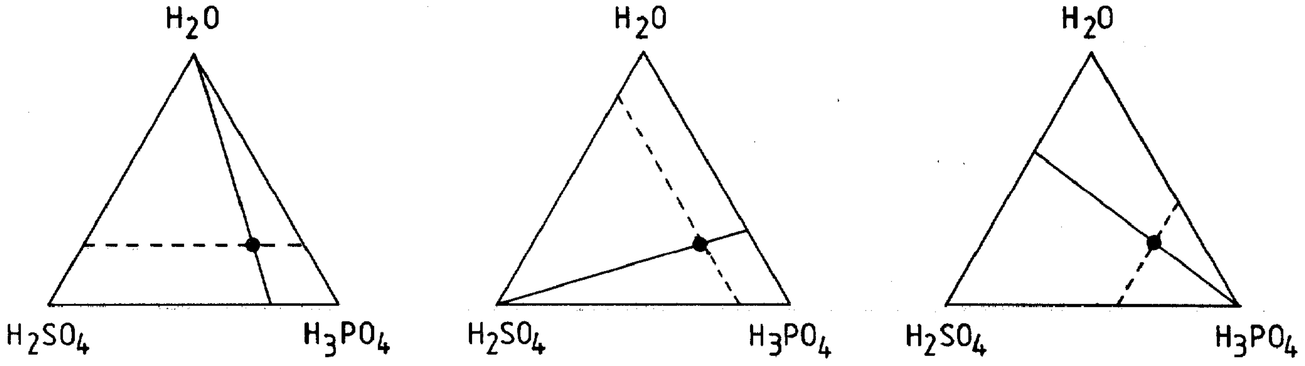

Figure 1: The three binary systems, in which the ternary system can be split up

The binary heats of mixing have to be calculated in each binary system at the following compositions:

$$\begin{aligned}
\Delta_1 H_{12} &= \Delta H_{12}(x_1,\ 1-x_1) \\
\Delta_1 H_{13} &= \Delta H_{13}(x_1,\ 1-x_1) \\
\Delta_1 H_{23} &= \Delta H_{23}(x_2/(x_2 + x_3),\ x_2/(x_2 + x_3))
\end{aligned}$$

$$\begin{aligned}
\Delta_2 H_{12} &= \Delta H_{12}(1-x_2, x_2) \\
\Delta_2 H_{13} &= \Delta H_{13}(x_1/(x_1 + x_3),\ x_1/(x_1 + x_3)) \\
\Delta_2 H_{23} &= \Delta H_{23}(1-x_2, x_2)
\end{aligned}$$

$$\begin{aligned}
\Delta_3 H_{12} &= \Delta H_{12}(x_1/(x_1 + x_2),\ x_1/(x_1 + x_2)) \\
\Delta_3 H_{13} &= \Delta H_{13}(1-x_3, x_3) \\
\Delta_3 H_{23} &= \Delta H_{23}(1-x_3, x_3)
\end{aligned}$$

in which x_1 = mole fraction water, Δ_1 = heats in binary system 1
x_2 = mole fraction H_2SO_4, Δ_2 = heats in binary system 2
x_3 = mole fraction H_3PO_4, Δ_3 = heats in binary system 3
ΔH_{12} = heat of mixing component 1 (water) and 2 (H_2SO_4), etc.

For each binary system a ternary heat of mixing can be obtained from the triplet of binary heats of mixing:

$$\Delta_1H_{123} = \frac{x_2}{x_2 + x_3} * \Delta_1H_{12} + \frac{x_3}{x_2 + x_3} * \Delta_1H_{13} + \sqrt{(1-x_1)} * \Delta_1H_{23}$$

$$\Delta_2H_{123} = \frac{x_1}{x_1 + x_3} * \Delta_2H_{12} + \frac{x_3}{x_1 + x_3} * \Delta_2H_{23} + \sqrt{(1-x_2)} * \Delta_2H_{13}$$

$$\Delta_3H_{123} = \frac{x_1}{x_1 + x_2} * \Delta_3H_{13} + \frac{x_2}{x_1 + x_2} * \Delta_3H_{23} + \sqrt{(1-x_3)} * \Delta_3H_{12}$$

The heat of mixing in the ternary system is then set equal to the mean value of the three ternary heats of mixing for the binary systems:

$$\Delta H_{123} = \frac{\Delta_1H_{123} + \Delta_2H_{123} + \Delta_3H_{123}}{3}$$

ΔH_{123} is given in calories per mol mixture.

The binary heats of mixing are given in the sections 8.6.8.1 to 8.6.8.3 Although all calculations are based on a temperature of 25 °C, these correlations may also be used at higher temperatures, because only a slight influence of the temperature was found [Knobeloch and Schwartz,1962]. The differences between the experimental values and the calculated values of the ternary heat of mixing are found to be smaller than 10 %, if the mole fraction of water in the system exceeds 0.5.

Binary heat of mixing in the H_3PO_4-H_2O system

From literature data [Farr,1950], the following expression was obtained for the heat of mixing of chemically pure phosphoric acid and water:

$$\Delta H_{13} = (F - 5.87) * x_3$$

in which $F = 56.968 * w - 2.9512 * w^2 + 0.09298 * w^3 - 1.1159 * 10^{-3} * w^4 + 4.8388 * 10^{-6} * w^5$
ΔH_{13} = heat of mixing in cal. per mol mixture
w = w% H_3PO_4 in solution and x_3 = mole fraction H_3PO_4 in solution

Binary heat of mixing in the H_2SO_4-H_2O system

The data given by Giauque e.a. [Giauque e.a.,1960], were used to derive the following expression for the heat of mixing of chemically pure sulphuric acid and water:

$$\Delta H_{12} = w * (100 - w) * (0.35801 - 5.639 * 10^{-4} * w + 4.3483 * 10^{-4} * w^2 - 8.5131 * 10^{-6} * w^3 + 8.2961 * 10^{-8} * w^4)$$

with w = w% H_2SO_4 in solution and ΔH_{12} = heat of mixing in cal. per mol mixture.

Binary heat of mixing in the H_3PO_4-H_2SO_4 system

The expression for calculating the binary heat of mixing of chemically pure phosphoric acid and sulphuric acid is [Knobeloch and Schwartz,1962]:

$$\Delta H_{23} = x_2 * x_3 * (1935 - 2641 * (x_2 - x_3) + 510.5 * (x_2 + x_3)^2)$$

in which x_2 = mole fraction sulphuric acid in solution
x_3 = mole fraction phosphoric acid in solution
ΔH_{23} = heat of mixing in cal per mol mixture

The last term in the correlation, given above, i.e. $510.5 * (x_2 + x_3)^2$, is probably a printing error in the original article, because $x_2 + x_3$ equals 1 in the binary system phosphoric-sulphuric acid. No significant error was found, however, in the ternary heat of mixing, if the above correlation is assumed to be correct.

TOTAL MASS AND HEAT BALANCES OF THE CTPA PROCESS

The total mass and heat balances of a 1000 ton P_2O_5 per day producing plant, operating according to the CTPA process was obtained by simultaneously solving 1268 linear or linearized equations. This large number of equations was necessary to obtain the composition of all process stream.
In figure 1 the largest part of the flowsheet of the CTPA process is given, while figure 2 shows the fluoride removal stage. The numbers given on the flowsheets, represent either an amount of heat, a process stream or a piece of equipment and are explained below. The composition of all process streams as well as the mass and heat streams are given in table 1.

LIST OF EQUIPMENT

A1	First fluoride scrubber and stripping column
A2	Second fluoride scrubber
C1	Direct contact condensor for the vapour from the flasher in the recrystallisation stage
C2	Direct contact condensor for the vapour from the flasher in the crystallisation stage
E1	Heat exchanger for heating the wash water of the HH washing stage
F1	Solid-liquid separation by gravity and a centrifuge after the digestion
F2a,2b	DH filtration and washing respectively
F3a,3b	HH filtration and washing respectively
R1	First digester
R2	Second digester
R3	Third digester

Q3R1-Q3R7,Q1T1 = Heat losses through the walls
Q4R1-Q4R7,Q2T1 = Power input by the stirrers
Q5R4,Q5R7,Q1F2,Q1F3 = heat of mixing
Q1E1 = HH wash water heating

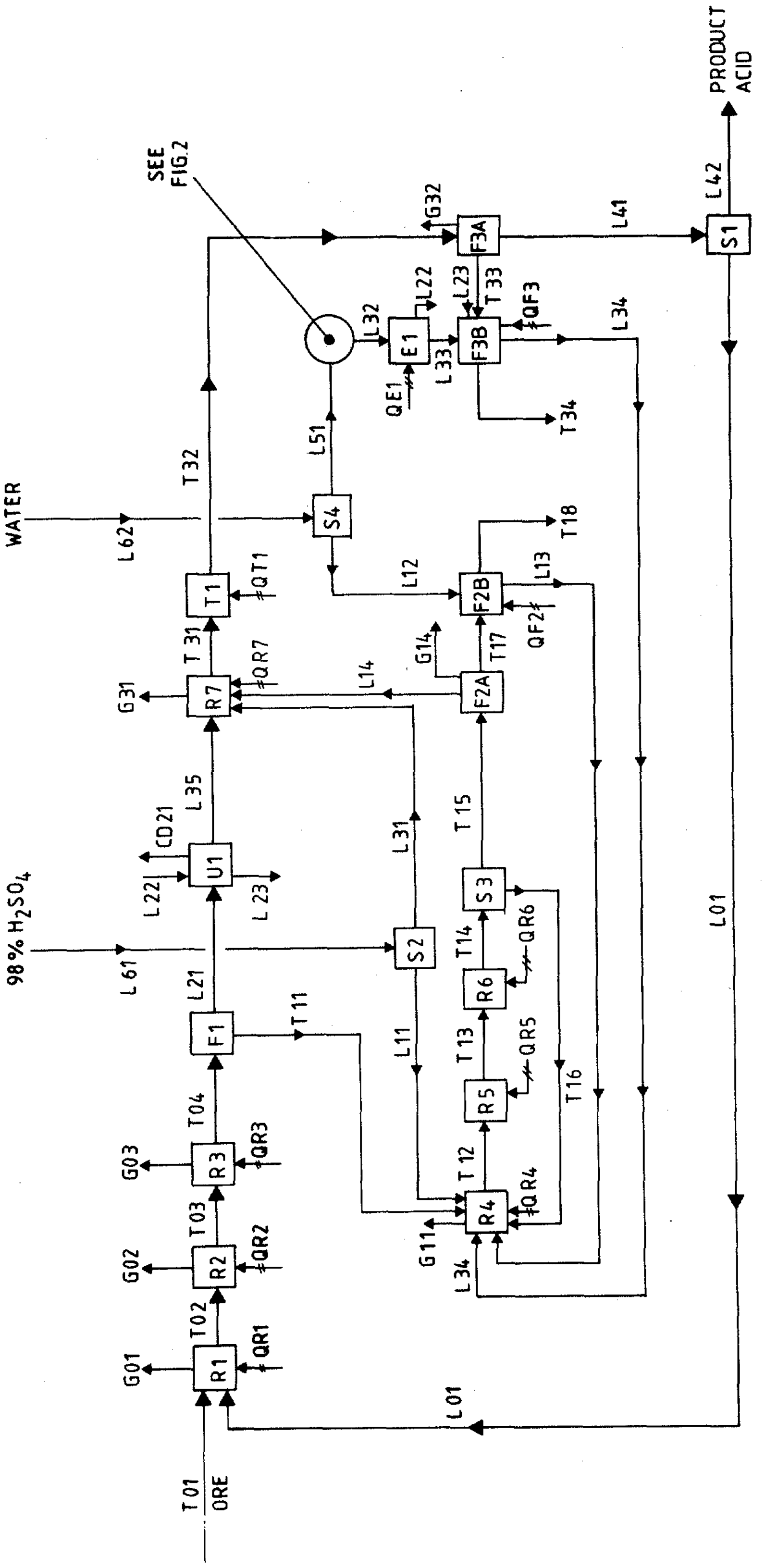

Figure 1: Flowsheet of the CTPA process (except the fluoride removal stage).

R4	First recrystalliser
R5	Second recrystalliser
R6	Third recrystalliser
R7	Crystalliser
S1	Product acid splitter
S2	Sulphuric acid splitter
S3	DH slurry recycle splitter
S4	Wash water splitter
T1	Filter feed tank for HH slurry
U1	Cadmium removal unit

LIST OF PROCESS STREAMS (KG/S)

CD = Cadmium
D, DR = Calcium sulphate dihydrate (DH)
E = Phosphate ore (soluble part)
G = Off gasses
H = Calcium sulphate hemihydrate (HH)
I = Inert (insoluble part of the ore)
K = liquid
L = liquid
S = clay
SC, SCR = scale
T01 = E01 + I01
T02 = E02 + H02 + I02 + K02 + SC02
T03 = E03 + H03 + I03 + K03 + SC03
T04 = E04 + H04 + I04 + K04 + SC04
T11 = E11 + H11 + I11 + K11 + SC11
T12 = D12 + H12 + I12 + K12 + SC12
T13 = D13 + H13 + I13 + K13 + SC13
T14 = D14 + I14 + K14 + SC14
T15 = D15 + I15 + K15 + SC15
T16 = D16 + I16 + K16 + SC16
T17 = D17 + I17 + K17 + SC17
T18 = D18 + I18 + K18 + SC18
T31 = H31 + K31
T32 = H32 + K32
T33 = H33 + K33
T34 = H34 + K34

LIST OF HEAT STREAMS (KJ/S)

QE1 =Q1E1
QF2 =Q1F2
QF3 =Q1F3
QR1 =Q1R1 + Q2R1 + Q3R1 + Q4R1
QR2 =Q1R2 + Q2R2 + Q3R2 + Q4R2
QR3 =Q1R3 + Q2R3 + Q3R3 + Q4R3
QR4 =Q1R4 + Q2R4 + Q3R4 + Q4R4 + Q5R4
QR5 =Q2R5 + Q3R5 + Q4R5
QR6 =Q2R6 + Q3R6 + Q4R6
QR7 =Q2R7 + Q3R7 + Q4R7 + Q5R7
QT1 =Q1T1 + Q2T1
Q1R1-Q1R4 = heat of digestion of phosphate ore
Q2R1-Q2R3,Q2R7 = heat of crystallisation of HH
Q2R4-Q2R6 = heat of recrystallisation of HH into DH

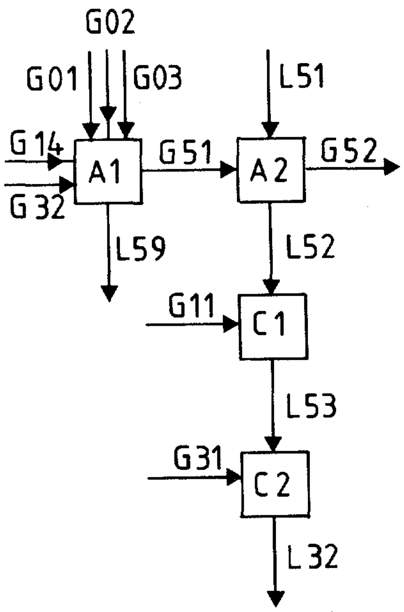

Figure 2: Flowsheet of the fluoride removal stage of the CTPA process.

See following pages 351 through 357 -

Table 1: The CTPA process: Composition of the process streams as well as the mass and heat streams.

```
                   CD21       D12       D13       D14       D15       D16       D17       D18       DR4       DR5

  1    P2O5           -     0.317     0.317     0.317     0.317     0.317     0.317     0.317     0.317     0.317
  2     CAO           -    31.854    31.745    31.643    31.643    31.643    31.643    31.643    32.111    30.336
  3   WATER           -    20.814    20.790    20.767    20.767    20.767    20.767    20.767    20.871    20.476
  4   FLUOR           -     2.734     3.157     3.552     3.552     3.552     3.552     3.552     1.736     8.628
  5     SO3           -    43.504    43.094    42.711    42.711    42.711    42.711    42.711    44.471    37.791
  6      SI           -         -         -         -         -         -         -         -         -         -
  7      AL           -     0.777     0.897     1.010     1.010     1.010     1.010     1.010     0.493     2.452
  8      NA           -         -         -         -         -         -         -         -         -         -
  9    REST           -         -         -         -         -         -         -         -         -         -

 13  %TOTAL       0.000   100.000   100.000   100.000   100.000   100.000   100.000   100.000   100.000   100.000
 14  TOTAAL       0.000    25.468    27.437    27.998    13.999    13.999    13.999    13.999    11.469     1.969
 15  VOLUME           -    11.016    11.867    12.110     6.055     6.055     6.055     6.055         -         -
 16     PVZ           -         -         -         -         -         -         -         -         -         -
 17   PRESS           -         -         -         -         -         -         -         -         -         -
 18    TEMP           -    59.594    60.000    59.957    59.957    59.957    59.882    36.521         -         -
 19  ENTHAL           -  1651.478  1791.899  1827.176   913.588   913.588   912.384   545.467   737.890   140.421
 20    FASE           -      GIPS      GIPS      GIPS      GIPS      GIPS      GIPS      GIPS      GIPS      GIPS
 21    CADM     645.777     0.163     0.163     0.163     0.163     0.163     0.163     0.163     0.163     0.163


                    DR6       E01       E02       E03       E04       E11       G01       G02       G03       G11

  1    P2O5       0.315    31.869    31.869    31.869    31.869    31.869         -         -         -         -
  2     CAO      26.674    51.313    51.313    51.313    51.313    51.313         -         -         -         -
  3   WATER      19.661     1.414     1.414     1.414     1.414     1.414    28.623    28.765    28.708    99.706
  4   FLUOR      22.849     4.242     4.242     4.242     4.242     4.242     2.484     2.451     2.409     0.236
  5     SO3      24.007     2.020     2.020     2.020     2.020     2.020         -         -         -         -
  6      SI           -     0.165     0.165     0.165     0.165     0.165     0.610     0.602     0.592     0.058
  7      AL       6.494     0.096     0.096     0.096     0.096     0.096         -         -         -         -
  8      NA           -     0.566     0.566     0.566     0.566     0.566         -         -         -         -
  9    REST           -     8.315     8.315     8.315     8.315     8.315    68.283    68.183    68.291         -

 13  %TOTAL     100.000   100.000   100.000   100.000   100.000   100.000   100.000   100.000   100.000   100.000
 14  TOTAAL       0.561    36.714     6.613     1.582     0.257     0.257     2.601     0.435     0.114     1.360
 15  VOLUME           -    13.598     2.449     0.586     0.095     0.095         -         -         -         -
 16     PVZ           -         -         -         -         -         -         -         -         -         -
 17   PRESS           -         -         -         -         -         -     1.000     1.000     1.000     0.137
 18    TEMP           -    15.000    92.254    92.337    92.309    92.309    92.254    92.337    92.309    55.594
 19  ENTHAL      35.277   393.107   471.487   112.873    18.336    18.336  2334.541   391.943   102.696  3535.909
 20    FASE        GIPS      ERTS      ERTS      ERTS      ERTS      ERTS       GAS       GAS       GAS       GAS
 21    CADM       0.164    21.212    21.212    21.212    21.212    21.212         -         -         -         -
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                    G14          G31          G32          G51          G52          H02          H03          H04          H11          H12

 1    P2O5        -            -            -            -            -                3.881        3.758        3.663        3.663        3.663
 2     CAO        -            -            -            -            -               37.876       37.353       36.979       36.979       36.979
 3   WATER       99.963       89.045       95.179       28.920       23.978        6.653        6.605        6.569        6.569        6.569
 4   FLUOR        0.030        8.795        3.870       -0.008        -                2.716        4.626        5.988        5.988        5.988
 5     SO3        -            -            -            -            -               48.102       46.344       45.099       45.099       45.099
 6      SI        0.007        2.160        0.951       -0.002        -            -            -            -            -            -    
 7      AL        -            -            -            -            -                0.772        1.315        1.702        1.702        1.702
 8      NA        -            -            -            -            -            -            -            -            -            -    
 9    REST        -            -            -           71.090       76.022        -            -            -            -            -    

13  %TOTAL      100.000      100.000      100.000      100.000      100.000      100.000      100.000      100.000      100.000      100.000
14  TOTAAL        0.005        0.392        0.010        3.026        2.829        9.127        9.755       10.098       10.098        2.020
15  VOLUME        -            -            -            -            -                3.324        3.553        3.677        3.677        0.735
16     PVZ        -            -            -            -            -            -            -            -            -            -    
17   PRESS        1.000        0.407        1.000        1.000        1.000        -            -            -            -            -    
18    TEMP       59.882       87.000       90.819       91.000       35.000       92.254       92.337       92.309       92.309       59.594
19  ENTHAL       12.954     1042.125       26.556     2492.099     1784.612      715.017      764.963      791.606      791.606       99.986
20    FASE          GAS          GAS          GAS          GAS          GAS         HEMI         HEMI         HEMI         HEMI         HEMI
21    CADM        -            -            -            -            -                0.030        0.030        0.029        0.029        0.029


                    H13          H31          H32          H33          H34          HR1          HR2          HR3          I01          I02

 1    P2O5        3.663        0.220        0.220        0.220        0.220        3.881        1.964        0.951        -            -    
 2     CAO       36.979       38.514       38.514       38.514       38.514       37.876       29.744       26.363        -            -    
 3   WATER        6.569        6.228        6.228        6.228        6.228        6.653        5.906        5.568        -            -    
 4   FLUOR        5.988        0.391        0.391        0.391        0.391        2.716       32.383       44.719        -            -    
 5     SO3       45.099       54.537       54.537       54.537       54.537       48.102       20.800        9.690        -            -    
 6      SI        -            -            -            -            -            -            -            -            -            -    
 7      AL        1.702        0.111        0.111        0.111        0.111        0.772        9.204       12.710        -            -    
 8      NA        -            -            -            -            -            -            -            -            -            -    
 9    REST        -            -            -            -            -            -            -            -          100.000      100.000

13  %TOTAL      100.000      100.000      100.000      100.000      100.000      100.000      100.000      100.001      100.000      100.000
14  TOTAAL        0.404       37.253       37.253       37.253       37.253        9.127        0.628        0.343        0.371        0.371
15  VOLUME        0.147       13.566       13.566       13.566       13.566        -            -            -                0.137        0.137
16     PVZ        -            -            -            -            -            -            -            -            -            -    
17   PRESS        -            -            -            -            -            -            -            -            -            -    
18    TEMP       60.000       91.000       90.844       90.819       76.313        -            -            -               15.000       92.254
19  ENTHAL       20.139     2876.327     2871.092     2870.256     2388.495      715.017       49.946       26.643        3.971       26.442
20    FASE         HEMI         HEMI         HEMI         HEMI         HEMI         HEMI         HEMI         HEMI       INERTS       INERTS
21    CADM        0.029        0.402        0.402        0.402        0.402        0.030        0.021        0.018        -            -    
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                 I03        I04        I11        I12        I13        I14        I15        I16        I17        I18

 1   P2O5          -          -          -          -          -          -          -          -          -          -
 2    CAO          -          -          -          -          -          -          -          -          -          -
 3  WATER          -          -          -          -          -          -          -          -          -          -
 4  FLUOR          -          -          -          -          -          -          -          -          -          -
 5    SO3          -          -          -          -          -          -          -          -          -          -
 6     SI          -          -          -          -          -          -          -          -          -          -
 7     AL          -          -          -          -          -          -          -          -          -          -
 8     NA          -          -          -          -          -          -          -          -          -          -
 9   REST    100.000    100.000    100.000    100.000    100.000    100.000    100.000    100.000    100.000    100.000

13 %TOTAL    100.000    100.000    100.000    100.000    100.000    100.000    100.000    100.000    100.000    100.000
14 TOTAAL      0.371      0.371      0.371      0.742      0.742      0.742      0.371      0.371      0.371      0.371
15 VOLUME      0.137      0.137      0.137      0.275      0.275      0.275      0.137      0.137      0.137      0.137
16    PVZ          -          -          -          -          -          -          -          -          -          -
17  PRESS          -          -          -          -          -          -          -          -          -          -
18   TEMP     92.337     92.309     92.309     59.594     60.000     59.957     59.957     59.957     59.882     36.521
19 ENTHAL     26.467     26.459     26.459     33.194     33.434     33.408     16.704     16.704     16.682      9.928
20   FASE     INERTS     INERTS     INERTS     INERTS     INERTS     INERTS     INERTS     INERTS     INERTS     INERTS
21   CADM          -          -          -          -          -          -          -          -          -          -


                 K02        K03        K04        K11        K12        K13        K14        K15        K16        K17

 1   P2O5     40.555     40.539     40.558     40.558     27.704     27.865     27.926     27.926     27.926     27.929
 2    CAO      4.108      4.825      5.000      5.000      0.043      0.043      0.043      0.043      0.043      0.043
 3  WATER     46.735     46.097     45.955     45.955     61.947     61.869     61.885     61.885     61.885     61.881
 4  FLUOR      2.551      2.512      2.470      2.470      2.131      2.058      1.951      1.951      1.951      1 951
 5    SO3      0.070      0.060      0.058      0.058      4.143      4.142      4.199      4.199      4.199      4.200
 6     SI      0.604      0.604      0.604      0.604      0.408      0.409      0.409      0.409      0.409      0.409
 7     AL      0.057      0.046      0.035      0.035      0.148      0.127      0.096      0.096      0.096      0.096
 8     NA      0.537      0.537      0.537      0.537      0.346      0.346      0.345      0.345      0.345      0.345
 9   REST      4.783      4.780      4.783      4.783      3.130      3.142      3.147      3.147      3.147      3.147

13 %TOTAL    100.000    100.000    100.000    100.000    100.000    100.000    100.000    100.000    100.000    100.000
14 TOTAAL    306.879    310.927    311.815     10.942     95.456     95.097     94.937     47.469     47.469      6.255
15 VOLUME    215.542    216.217    216.260      7.589     72.903     72.531     72.312     36.156     36.156      4.764
16    PVZ     -7.103     -8.370     -8.679          -      5.000      4.999      5.069          -          -          -
17  PRESS      0.496      0.497      0.497          -          -          -          -          -          -          -
18   TEMP     92.254     92.337     92.309     92.309     59.594     60.000     59.957     59.957     59.957     59.882
19 ENTHAL  68762.187  69154.062  69161.375   2426.897  16568.164  16592.516  16541.691   8270.844   8270.848   1088.382
20   FASE     LIQUID     LIQUID     LIQUID     LIQUID     LIQUID     LIQUID     LIQUID     LIQUID     LIQUID     LIQUID
21   CADM      5.834      6.101      6.174      6.174      3.259      3.268      3.273      3.273      3.273      3.273
```

		K18	K31	K32	K33	K34	L01	L11	L12	L13	L14
1	P2O5	-	39.999	39.999	40.000	-	40.000	0.000	-	17.005	27.929
2	CAO	-	0.214	0.214	0.214	-	0.214	-	-	0.026	0.043
3	WATER	100.000	50.114	50.114	50.113	100.000	50.113	20.000	100.000	76.790	61.881
4	FLUOR	-	2.420	2.420	2.420	-	2.420	-	-	1.188	1.951
5	SO3	-	1.388	1.388	1.388	-	1.388	80.000	-	2.557	4.200
6	SI	-	0.594	0.594	0.594	-	0.594	-	-	0.249	0.409
7	AL	-	0.031	0.031	0.031	-	0.031	-	-	0.058	0.096
8	NA	-	0.528	0.528	0.528	-	0.528	-	-	0.210	0.345
9	REST	-	4.712	4.712	4.712	-	4.712	-	-	1.916	3.147
13	%TOTAL	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000
14	TOTAAL	6.255	332.950	332.950	15.965	15.965	288.040	3.653	10.273	10.273	41.209
15	VOLUME	6.314	237.775	237.775	11.402	16.399	205.700	1.982	10.274	8.766	31.387
16	PVZ	-	1.325	-	-	-	1.325	-	-	-	-
17	PRESS	-	-	-	-	-	-	-	-	-	-
18	TEMP	36.521	91.000	90.844	90.819	76.313	90.819	15.000	15.000	36.521	59.882
19	ENTHAL	960.982	77899.125	77760.375	3727.606	5146.891	67251.375	84.871	647.848	1208.569	7170.746
20	FASE	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID
21	CADM	-	4.000	4.000	4.000	-	4.000	-	-	1.993	3.273

		L21	L22	L23	L31	L32	L33	L34	L35	L41	L42
1	P2O5	40.558	-	10.000	0.000	-	-	24.132	40.503	40.000	40.000
2	CAO	5.000	-	-	-	-	-	0.124	5.005	0.214	0.214
3	WATER	45.955	99.829	89.846	20.000	99.829	99.829	69.982	45.998	50.113	50.113
4	FLUOR	2.470	0.137	0.123	-	0.137	0.137	1.535	2.473	2.420	2.420
5	SO3	0.058	-	-	80.000	-	-	0.803	0.058	1.388	1.388
6	SI	0.604	0.034	0.030	-	0.034	0.034	0.377	0.605	0.594	0.594
7	AL	0.035	-	-	-	-	-	0.018	0.035	0.031	0.031
8	NA	0.537	-	-	-	-	-	0.305	0.537	0.528	0.528
9	REST	4.783	-	-	-	-	-	2.724	4.787	4.712	4.712
13	%TOTAL	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000
14	TOTAAL	300.873	2.500	2.778	28.791	27.336	24.836	27.614	300.595	316.975	28.935
15	VOLUME	208.672	2.550	2.601	15.620	27.875	25.329	22.851	208.575	226.363	20.664
16	PVZ	-	-	-	-	-	-	-	-	-	-
17	PRESS	-	-	-	-	-	-	-	-	-	-
18	TEMP	92.309	60.000	60.000	15.000	59.761	60.000	76.313	92.387	90.819	90.819
19	ENTHAL	66734.437	632.334	578.108	668.913	6886.582	6281.957	6409.469	66788.625	74007.000	6755.687
20	FASE	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID
21	CADM	6.174	-	-	-	-	-	2.313	4.032	4.000	4.000

		L51	L52	L53	L59	L61	L62	S01	S02	S03	SC02
1	P2O5	-	-	-	-	0.000	-	-	-	-	-
2	CAO	-	-	-	-	-	-	-	-	-	-
3	WATER	100.000	100.001	99.986	30.000	20.000	100.000	-	-	-	-
4	FLUOR	-	-0.001	0.011	56.197	-	-	-	-	-	60.638
5	SO3	-	-	-	-	80.000	-	-	-	-	-
6	SI	-	0.000	0.003	13.803	-	-	21.000	21.000	21.000	14.894
7	AL	-	-	-	-	-	-	20.000	20.000	20.000	-
8	NA	-	-	-	-	-	-	-	-	-	24.468
9	REST	-	-	-	-	-	-	59.000	59.000	59.000	-
13	%TOTAL	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000
14	TOTAAL	25.387	25.584	26.944	0.140	32.444	35.660	0.782	0.141	0.034	0.175
15	VOLUME	25.391	25.659	27.377	-	17.602	35.665	-	-	-	-
16	PVZ	-	-	-	-	-	-	-	-	-	-
17	PRESS	-	-	-	-	-	-	-	-	-	-
18	TEMP	15.000	21.462	51.500	-	15.000	15.000	15.000	92.254	92.337	92.254
19	ENTHAL	1601.061	2308.548	5844.457	376.591	753.785	2248.909	11.028	12.216	2.924	11.909
20	FASE	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	KLEI	KLEI	KLEI	SCAL
21	CADM	-	-	-	-	-	-	-	-	-	-

		SC03	SC04	SC11	SC12	SC13	SC14	SC15	SC16	SC17	SC18
1	P2O5	-	-	-	-	-	-	-	-	-	-
2	CAO	-	-	-	-	-	-	-	-	-	-
3	WATER	-	-	-	-	-	-	-	-	-	-
4	FLUOR	60.638	60.638	60.638	60.638	60.638	60.638	60.638	60.638	60.638	60.638
5	SO3	-	-	-	-	-	-	-	-	-	-
6	SI	14.894	14.894	14.894	14.894	14.894	14.894	14.894	14.894	14.894	14.894
7	AL	-	-	-	-	-	-	-	-	-	-
8	NA	24.468	24.468	24.468	24.468	24.468	24.468	24.468	24.468	24.468	24.468
9	REST	-	-	-	-	-	-	-	-	-	-
13	%TOTAL	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000
14	TOTAAL	0.202	0.216	0.216	0.440	0.446	0.449	0.224	0.224	0.224	0.224
15	VOLUME	-	-	-	-	-	-	-	-	-	-
16	PVZ	-	-	-	-	-	-	-	-	-	-
17	PRESS	-	-	-	-	-	-	-	-	-	-
18	TEMP	92.337	92.309	92.309	59.594	60.000	59.957	59.957	59.957	59.882	36.521
19	ENTHAL	13.831	14.631	14.688	19.641	20.067	20.168	10.089	10.089	10.066	6.145
20	FASE	SCAL	SCAL	SCAL	SCAL	SCAL	SCAL	SCAL	SCAL	SCAL	SCAL
21	CADM	-	-	-	-	-	-	-	-	-	-

```
                 SCR1      SCR2      SCR3      SCR4      SCR5      SCR6      Q1E1      Q1F2      Q1F3      Q1R1

 1   P2O5          -         -         -         -         -         -         -         -         -         -
 2    CAO          -         -         -         -         -         -         -         -         -         -
 3  WATER          -         -         -         -         -         -         -         -         -         -
 4  FLUOR     60.638    60.638    60.638     0.000    60.638    60.638         -         -         -         -
 5    SO3          -         -         -         -         -         -         -         -         -         -
 6     SI     14.894    14.894    14.894     0.000    14.894    14.894         -         -         -         -
 7     AL          -         -         -         -         -         -         -         -         -         -
 8     NA     24.468    24.468    24.468     0.000    24.468    24.468         -         -         -         -
 9   REST          -         -         -         -         -         -         -         -         -         -

13 %TOTAL    100.000   100.000   100.000     0.000   100.000   100.000     0.000     0.000     0.000     0.000
14 TOTAAL      0.175     0.027     0.013     0.000     0.006     0.003     0.000     0.000     0.000     0.000
15 VOLUME          -         -         -         -         -         -         -         -         -         -
16    PVZ          -         -         -         -         -         -         -         -         -         -
17  PRESS          -         -         -         -         -         -         -         -         -         -
18   TEMP          -         -         -         -         -         -         -         -         -         -
19 ENTHAL     11.909     1.701     0.625    -5.375     0.402     0.098    27.711    55.719   486.938  3010.151
20   FASE       SCAL      SCAL      SCAL      SCAL      SCAL      SCAL         -         -         -         -
21   CADM          -         -         -         -         -         -         -         -         -         -


                 Q2R1      Q3R1      Q4R1      Q1R2      Q2R2      Q3R2      Q4R2      Q1R3      Q2R3      Q3R3

 1   P2O5          -         -         -         -         -         -         -         -         -         -
 2    CAO          -         -         -         -         -         -         -         -         -         -
 3  WATER          -         -         -         -         -         -         -         -         -         -
 4  FLUOR          -         -         -         -         -         -         -         -         -         -
 5    SO3          -         -         -         -         -         -         -         -         -         -
 6     SI          -         -         -         -         -         -         -         -         -         -
 7     AL          -         -         -         -         -         -         -         -         -         -
 8     NA          -         -         -         -         -         -         -         -         -         -
 9   REST          -         -         -         -         -         -         -         -         -         -

13 %TOTAL      0.000     0.000     0.000     0.000     0.000     0.000     0.000     0.000     0.000     0.000
14 TOTAAL      0.000     0.000     0.000     0.000     0.000     0.000     0.000     0.000     0.000     0.000
15 VOLUME          -         -         -         -         -         -         -         -         -         -
16    PVZ          -         -         -         -         -         -         -         -         -         -
17  PRESS          -         -         -         -         -         -         -         -         -         -
18   TEMP          -         -         -         -         -         -         -         -         -         -
19 ENTHAL   1825.406  -193.000    32.000   503.119   125.652  -193.000    32.000   132.454    68.594  -193.000
20   FASE          -         -         -         -         -         -         -         -         -         -
21   CADM          -         -         -         -         -         -         -         -         -         -
```

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              Q4R3      Q1R4      Q2R4      Q3R4      Q4R4      Q5R4      Q2R5      Q3R5      Q4R5      Q2R6

 1    P2O5     -         -         -         -         -         -         -         -         -         -
 2     CAO     -         -         -         -         -         -         -         -         -         -
 3   WATER     -         -         -         -         -         -         -         -         -         -
 4   FLUOR     -         -         -         -         -         -         -         -         -         -
 5     SO3     -         -         -         -         -         -         -         -         -         -
 6      SI     -         -         -         -         -         -         -         -         -         -
 7      AL     -         -         -         -         -         -         -         -         -         -
 8      NA     -         -         -         -         -         -         -         -         -         -
 9    REST     -         -         -         -         -         -         -         -         -         -

13 %TOTAL    0.000     0.000     0.000     0.000     0.000     0.000     0.000     0.000     0.000     0.000
14 TOTAAL    0.000     0.000     0.000     0.000     0.000     0.000     0.000     0.000     0.000     0.000
15 VOLUME      -         -         -         -         -         -         -         -         -         -
16     PVZ     -         -         -         -         -         -         -         -         -         -
17   PRESS     -         -         -         -         -         -         -         -         -         -
18    TEMP     -         -         -         -         -         -         -         -         -         -
19 ENTHAL   32.000    25.700   807.861  -124.000    48.000   958.467   161.572  -124.000    48.000    40.393
20    FASE     -         -         -         -         -         -         -         -         -         -
21    CADM     -         -         -         -         -         -         -         -         -         -


              Q3R6      Q4R6      Q2R7      Q3R7      Q4R7      Q5R7      Q1T1      Q2T1

 1    P2O5     -         -         -         -         -         -         -         -
 2     CAO     -         -         -         -         -         -         -         -
 3   WATER     -         -         -         -         -         -         -         -
 4   FLUOR     -         -         -         -         -         -         -         -
 5     SO3     -         -         -         -         -         -         -         -
 6      SI     -         -         -         -         -         -         -         -
 7      AL     -         -         -         -         -         -         -         -
 8      NA     -         -         -         -         -         -         -         -
 9    REST     -         -         -         -         -         -         -         -

13 %TOTAL    0.000     0.000     0.000     0.000     0.000     0.000     0.000     0.000
14 TOTAAL    0.000     0.000     0.000     0.000     0.000     0.000     0.000     0.000
15 VOLUME      -         -         -         -         -         -         -         -
16     PVZ     -         -         -         -         -         -         -         -
17   PRESS     -         -         -         -         -         -         -         -
18    TEMP     -         -         -         -         -         -         -         -
19 ENTHAL -124.000    48.000  7450.551  -192.000    48.000  -117.249  -192.000    48.000
20    FASE     -         -         -         -         -         -         -         -
21    CADM     -         -         -         -         -         -         -         -
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EFFECTS OF PHOSPHORIC ACID ON DRYING AND DEHYDRATION OF CALCIUM SULFATE FILTER CAKES

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ABSTRACT

Calcium sulfate precipitated during the production of phosphoric acid may contain significant amounts of phosphate present as lattice P_2O_5, secondary phosphate precipitates, or free phosphoric acid. When the calcium sulfate from the filter is dried at 70°C to remove free water, portions of the calcium sulfate initially present as hemihydrate and/or gypsum may be converted to anhydrite, with the extent of dehydration depending on the amount of free phosphoric acid in the cake. The presence of phosphoric acid also causes evolution of fluorine and silica in the subsequent determination of combined water at 500°C. Both the dehydration at 70°C and the evolution, of fluorine and silica at 500°C increase with increasing amounts of phosphoric acid in the cake. Plots and figures are used to illustrate these effects, and a possible explanation is presented based on vapor pressure changes.

INTRODUCTION

In the operation of a phosphoric acid research facility, samples of calcium sulfate filter cake are collected and prepared for analysis by two methods. In the first method a weighed sample of the wet cake is dried at 70°C in a forced-draft oven for 12 hours to give a "dry cake." Analytical data from the dry cake then are used to calculate yields and impurity distributions. In the second method a weighed sample of the wet cake is washed successively with water, isopropanol, and acetone and then air dried at room temperature to produce what is called the "leached cake." A comparison of the phosphate analysis of the two cakes gives an indication of the washing efficiency of the cake on the filter. Portions of the dry and leached cakes then are heated at 500°C to determine the combined water content by weight loss and to prepare homogeneous anhydrite matrices for X-ray fluorescence (XRF) analysis.

The combined water in the dry and leached cakes should be approximately the same, and for most samples this was true. However, for some samples there was a wide difference in combined water, with the combined water in the dry cake being much lower than that in the corresponding leached cake.

The major difference expected between the dry and leached cakes produced by these procedures was that soluble P_2O_5 had been removed from the leached cake. This difference was readily confirmed by chemical analysis, which showed that the P_2O_5 in the dry cake ranged from 0.91 to 13.68%

P_2O_5; in the corresponding leached cakes the range was only from 0.70 to 1.21% P_2O_5. It also was anticipated that the leaching process could remove any soluble fluorosilicate salts which might be present, but it was not expected that either of the procedures would materially affect the combined water content of the cake.

EFFECT OF P_2O_5 ON COMBINED WATER

Figure 1 shows that the ratio of combined water in the dry cakes to the combined water in the leached cakes depended on the amount of P_2O_5 in the dry cake. The samples containing less than 2% P_2O_5 had a mean combined water ratio of 0.996, while the samples containing over 2% P_2O_5 had a mean ratio of only 0.590. Thus, the combined water results for the two cakes are virtually identical when the P_2O_5 content of the dry cake is 2% or less. At higher P_2O_5 levels, however, the dry cakes have significantly smaller weight losses upon dehydration.

The reduction in combined water values for the dry cakes is no doubt caused by partial dehydration during the drying procedure in the 70°C oven. This was surprising because thermograms of pure gypsum contained endothermic peaks at 155° and 197°C, which corresponded to the loss of water by the dihydrate and hemihydrate, respectively (Meredith, 1965; Ljunggren, 1960). Consequently, we did not expect gypsum to lose water of hydration at a temperature of 70°C. Further study of the literature, however, indicated that gypsum may dehydrate below 100°C under certain conditions. The nature of the sample (that is, the purity, crystallinity, habit, and so forth),

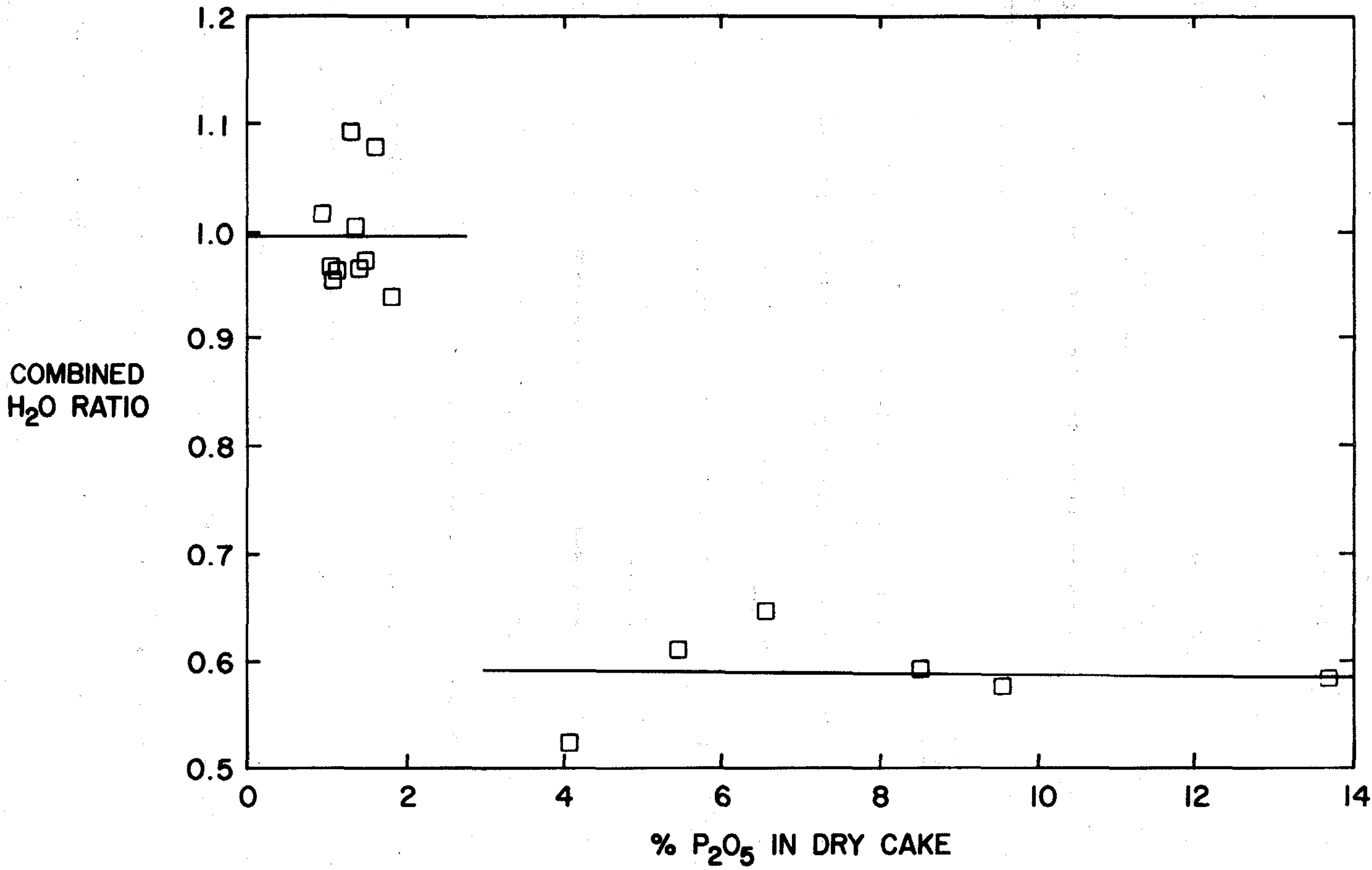

Figure 1. Effect of P_2O_5 on combined H20 ratio of dry to leached cakes.

along with the experimental conditions (such as atmosphere, heating rate, and particle size), are important variables in the dehydration, according to Wiedemann and Bayer (1975).

In our case, the explanation for the dehydration at 70°C must lie in the high acidity produced as the free water was removed from the cake. For those cakes in which the P_2O_5 was below 2%, most of the P_2O_5 was present as water-insoluble species so that as the free water was removed, solutions of high acidity were not produced and the calcium sulfate hydrates were stable.

X-ray diffraction analysis confirmed the presence of anhydrite in the dry cakes, and Figure 2 shows that the amount of anhydrite was directly proportional to the amount of P_2O_5 in the cakes. The X-ray data indicated that anhydrite was present in all of the samples, which supports the supposition that dehydration of gypsum and hemihydrate can occur simultaneously. In most of the samples the anhydrite was present as fine-grained amorphous material, which was difficult to identify by optical microscopy.

To check the effects observed with the filter cakes, a series of tests was carried out to determine the effects of added phosphoric acid on the drying of gypsum slurries at 70°C. The slurries were prepared by mixing reagent gypsum, water, and reagent phosphoric acid. The slurries were dried to remove the free water and then calcined at 500°C to determine the combined water. No dehydration of the gypsum occurred in the absence of phosphoric acid; but the presence of 1-10% P_2O_5 in the samples caused distinct changes in the combined water, as shown in Figure 3. The gypsum samples which

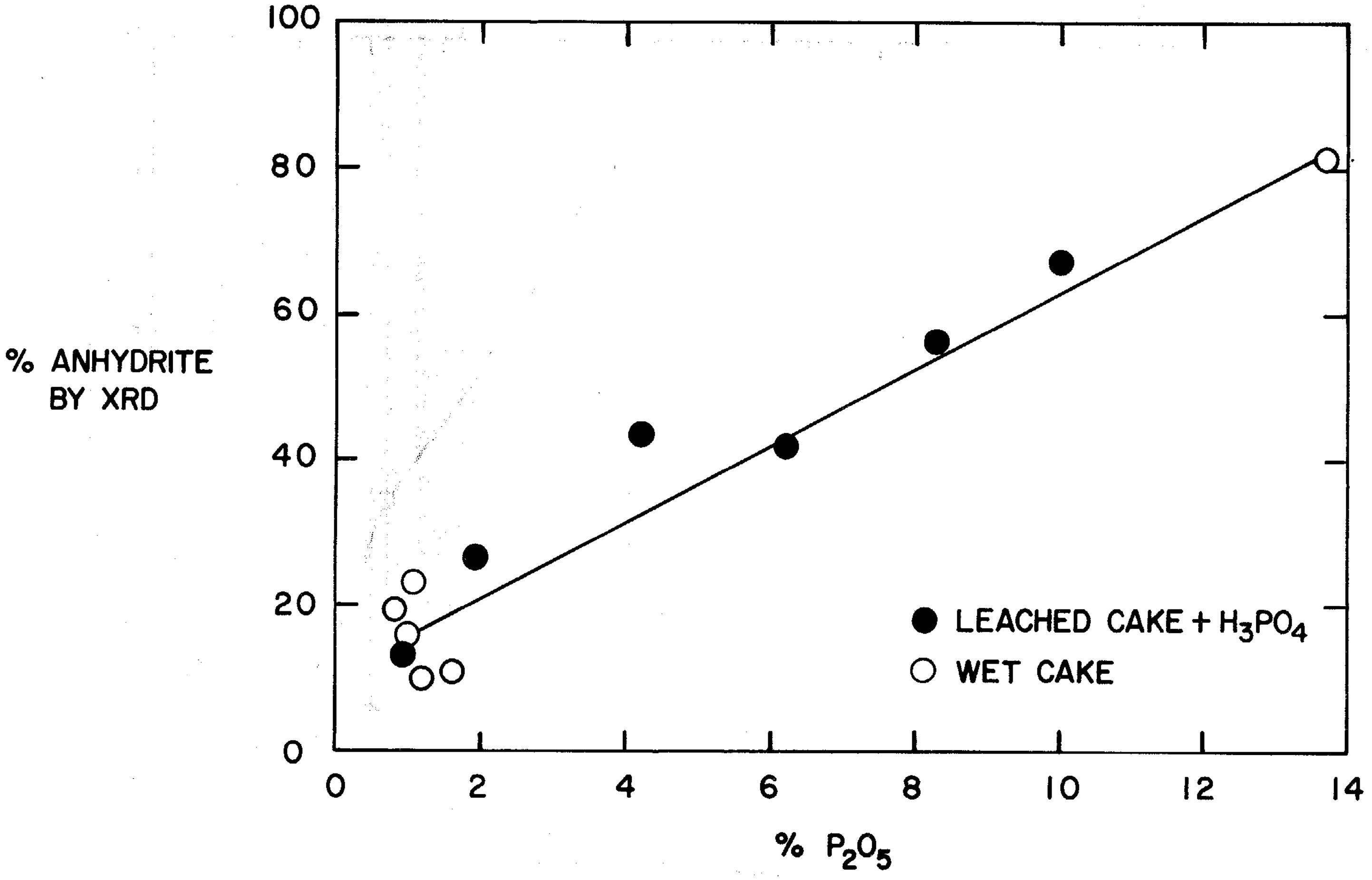

Figure 2. Effect of P_2O_5 on formation of anhydrite from filter cakes at 70°C.

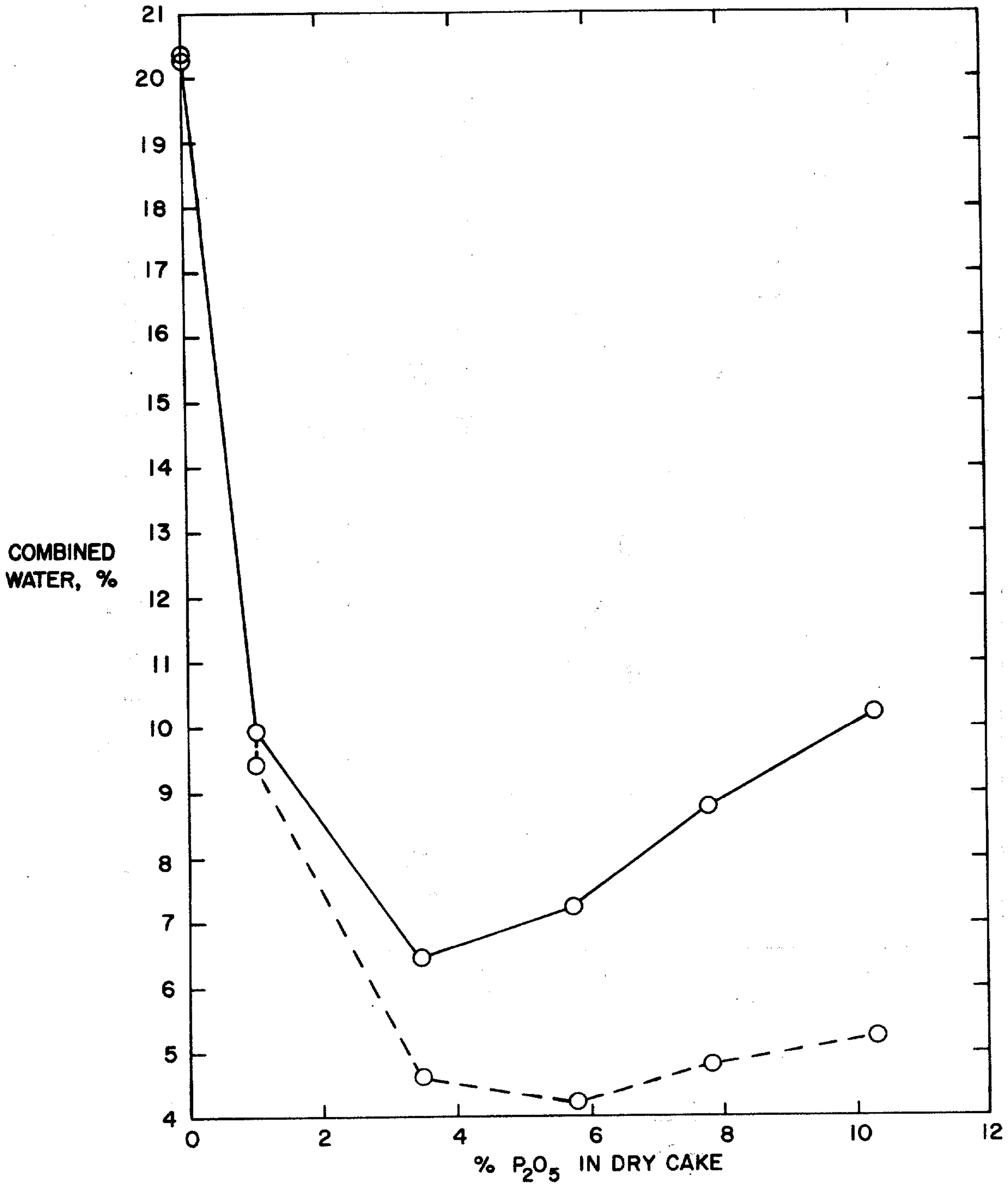

Figure 3. Effect of P_2O_5 on combined H_2O of gypsum dried at 70°C.

contained about 1% P_2O_5 or more show a marked decrease in combined water content upon dehydration at 500°C. This confirms our suggestion that the free phosphoric acid is responsible for the dehydration during the drying process rather than other forms of P_2O_5. Material balance calculations for P_2O_5 and water showed that no P_2O_5 was volatilized and that the total of the weight losses at 70° and 500°C ranged from 100.7 to 102.6% of the calculated values.

The mechanism by which hydrates of calcium sulfate are dehydrated in the presence of phosphoric acid is presumably based on vapor pressure effects. At 70°C the vapor pressures for gypsum and hemihydrate are about 160 and 5 torr, respectively. In the initial slurries the phosphoric acid concentration in the liquid phase of the slurry ranged from 1-10%. At these concentrations the vapor pressure of water over the acid was greater than 160 torr, and the calcium sulfate hydrates in the slurry were stable. As the free water in the system evaporated, the concentration of phosphoric acid in the liquid phase increased, with a consequent lowering of the partial pressure of water over the system. When the partial pressure of water over the system fell below 160 torr, gypsum began to lose water to the system. This occurred when the phosphoric acid concentration in the liquid phase approached 60%. Evidently, the phosphoric acid accelerated the dehydration of gypsum and hemihydrate by absorption of water vapor driven out of the cake, with subsequent removal of the water vapor from the acid by air flowing over the samples.

Theoretically, the loss of water from the gypsum would continue until hemihydrate was produced. The hemihydrate would be stable until the partial pressure of water over the system fell to about 5 torr, after which the hemihydrate would begin to lose water and be converted to anhydrite. This would occur when the phosphoric acid concentration approached 85% in the liquid phase. The process has been described as a stepwise decomposition, but the concentration of the acid increased continuously and it was possible for both steps to occur simultaneously.

The solid line in Figure 3 is based on the assumption that the total weight loss at 500°C was due to combined water remaining in the dry cake. The apparent increase in combined water at the higher P_2O_5 levels is believed to be due to a reduced rate of evaporation over the stronger acid rather than an indication of rehydration. As one might expect, the stronger acid solution tended to lose less water than the weaker solutions during the U-hour time periods used in these tests. The broken line in Figure 3 represents a correction made by assuming that the phosphoric acid remaining in the cakes was 90% H_3PO_4 and that it was converted to metaphosphoric acid, with the loss of one mole of water plus the free water that was in the orthophosphoric acid. This amount of water then was subtracted from the total weight loss at 500°C, and the combined water due to hydrates of $CaSO_4$ was recalculated. The corrected curve shows that the combined water in the 70°C samples was as low as about 4.5%. This confirms the supposition that the dehydration did not stop at hemihydrate, which contained 6.20% combined water.

Similar effects of phosphoric acid on the drying of gypsum were reported by Savinkova et al. (1985). They found that the presence of phosphoric acid causes the formation of hemihydrate at 80°-90°C and anhydrite at 120°-140°C. Their tests, however, were carried out in fluidized beds for periods of 15-45 minutes and the results are not directly comparable to ours.

EFFECT OF P_2O_5 ON FLUORINE AND SILICA EVOLUTION

The loss of fluorine, silica, and water upon heating a typical leached cake at 500°C for 11-120 minutes was investigated. Figure 4 shows that the total weight loss for this particular sample, which contained 0.93% P_2O_5, is a function of time. During the first 20 minutes the cake lost weight rapidly, but after about 25 minutes the weight loss remained virtually constant at 14%. The fraction of weight loss due to water was 93.9%. and the remaining 6.1% of the weight loss was due to volatilization of fluorides and silica (Figure 5). The fraction of fluoride which volatilized increased with calcination time. It increased from 24.2% after 4 minutes to 42.4% after 120 minutes; however, the fraction of the total weight loss due to fluoride evolution increased from 1.5 to only 2.5% over the same period. The data for the evolution of silica were somewhat erratic but, in general, the evolution of silica increased slowly as calcination time increased. The percentage of silica evolved averaged 9%, and its contribution to the total weight loss was around 3.5%.

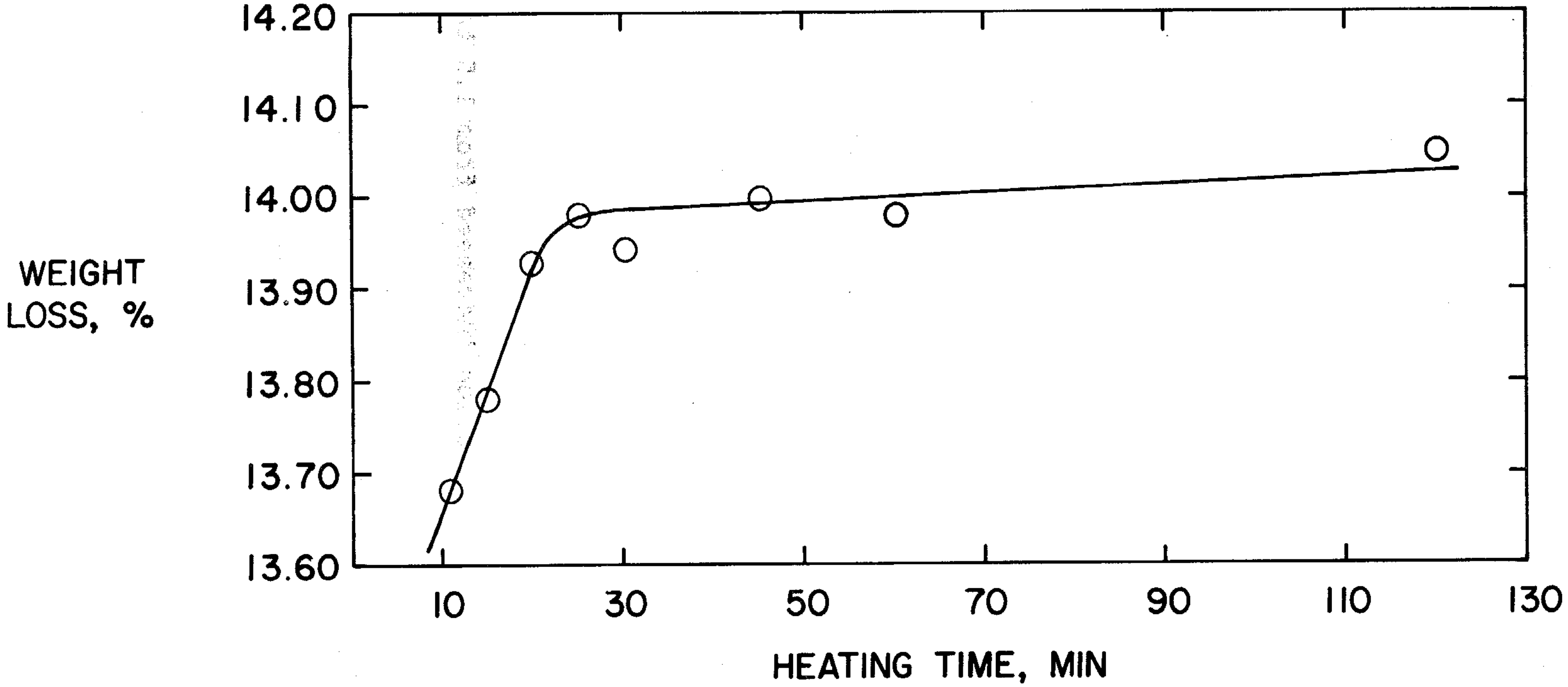

Figure 4. Effect of heating time on weight loss of filter cakes at 500°C.

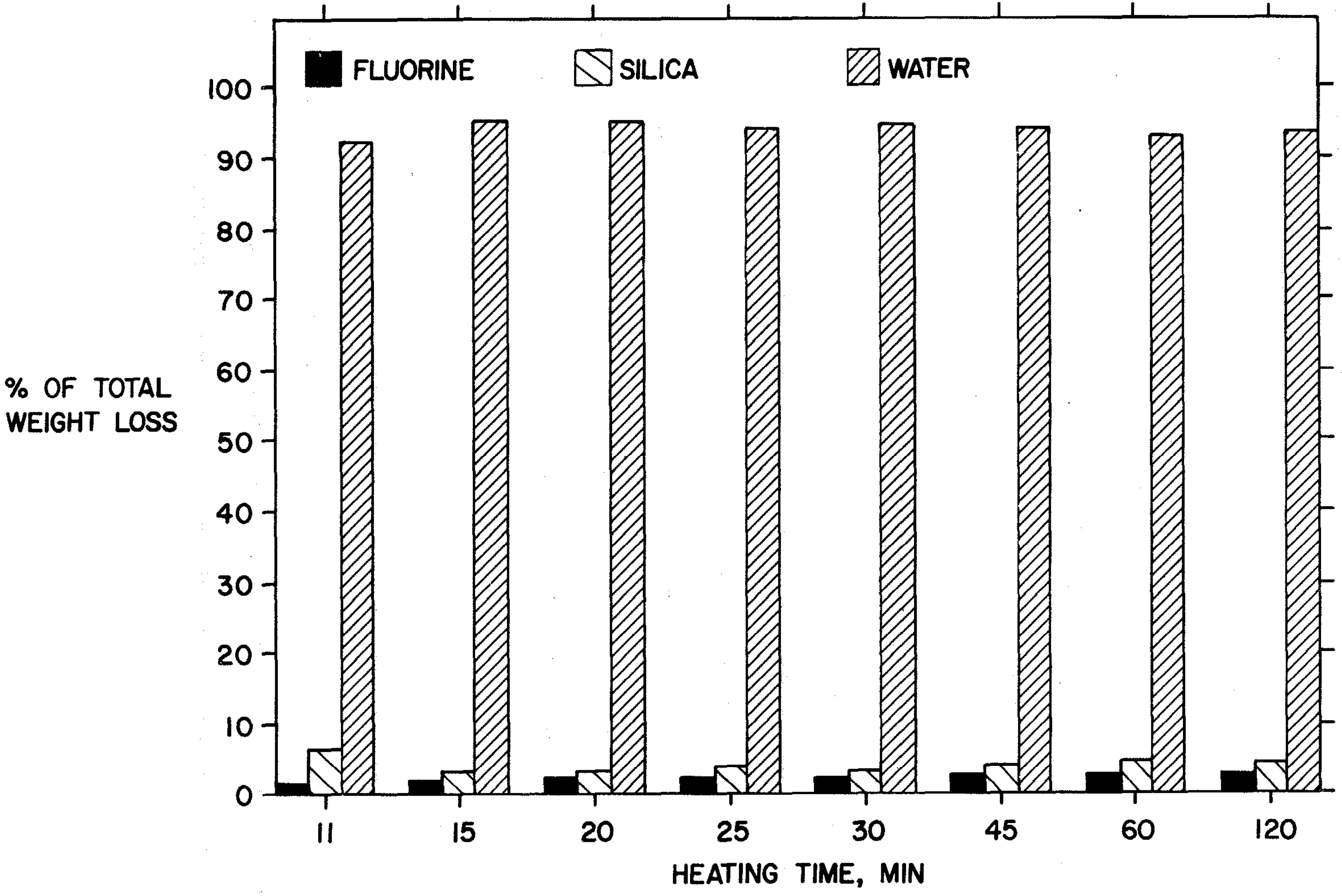

Figure 5. Distribution of volatile components upon heating filter cakes at 500°C.

The mole ratio of fluorine to silica evolved ranged from 1.67 to 2.13, with a mean value of 1.88 over the 15- to 120-minute calcination span. The precise mechanism by which fluoride and silica were evolved is not known, but it cannot be the simple volatilization and decomposition of fluorosilicic acid, which requires that fluoride and silica be evolved in a mole ratio of six to one. Furthermore, any fluorosilicate salts which may be present normally decompose at 500°C with the release of silicon tetrafluoride and formation of the corresponding metallic fluoride. This indicates that an unidentified silicon species was expelled from the sample.

Other tests showed that the evolution of fluoride was related to the P_2O_5 content of the filter cake, as shown in Figure 6. Samples containing less than 2% P_2O_5 lost 22-42% of their fluoride during the calcination treatment. On the other hand, 62-78% of the fluoride was lost when the P_2O_5 content was over 2%. It seems likely that fluoride complexes in the cake are decomposed by the presence of phosphoric acid to hydrofluoric acid, which then is easily volatilized; the increase in fluoride evolution is due to a combination of acidic and thermal decomposition of the fluoride-containing components in the cake. A recent report in the Russian literature (Borisov et al., 1983) confirms our results, as shown by the triangular points in Figure 6. Therefore, when filter cakes contain over about 2% P_2O_5, the drying and dehydration procedure may overestimate the combined water content by the increased amount of fluorine evolved.

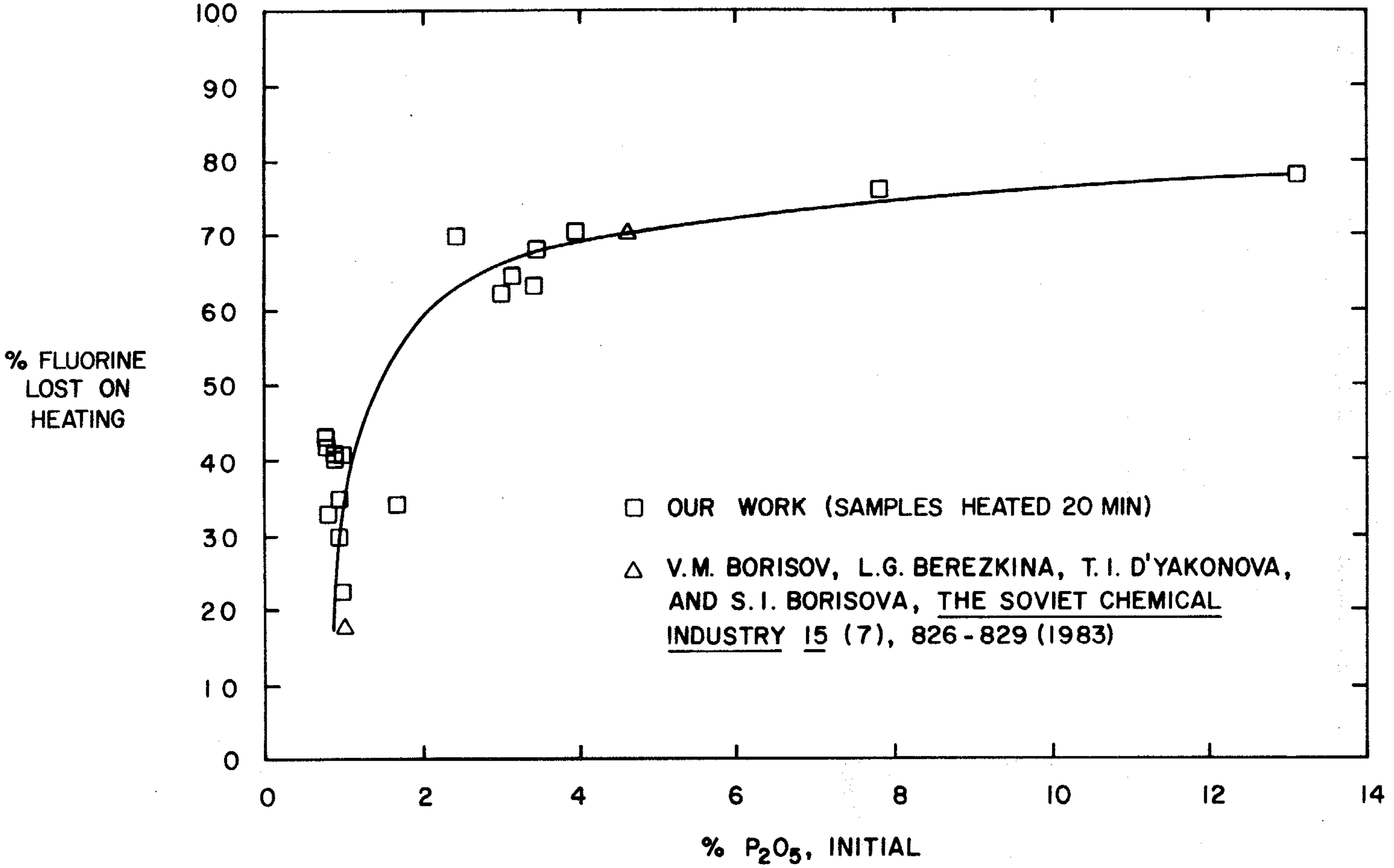

Figure 6. Effect of P_2O_5 on loss of fluorine in dehydration of filter cakes at 500°C.

Figure 1. Effect of P_2O_5 on combined H_2O ratio of dry to leached cakes.

Figure 2. Effect of P_2O_5 on formation of anhydrite from filter cakes at 70°C.

Figure 3. Effect of P_2O_5 on combined H_2O of gypsum dried at 70°C.

Figure 4. Effect of heating time on weight loss of filter cakes at 500°C.

Figure 5. Distribution of volatile components upon heating filter cakes at 500°C.

Figure 6. Effect of P_2O_5 on loss of fluorine in dehydration of filter cakes at 500°C.

CONCLUSIONS

It is concluded that the procedures used to prepare dry and leached cakes from the wet filter cake produced during the operation of a phosphoric acid unit are satisfactory for most samples. To avoid misleading data, the following points should be given due consideration:

1. Phosphoric acid in the filter cakes can cause the formation of anhydrite in drying treatments at temperatures as low as 70°C.
2. The presence of phosphoric acid in the filter cake promotes the evolution of silicon and fluorine during the dehydration treatment at 500°C.
3. Both of these effects increase with increasing amounts of phosphoric acid left in the cake.
4. Erroneous results for combined water may be obtained if the P_2O_5 content of the cake exceeds about 2%.
5. The bulk of the free acid in the cakes can be removed by a water-isopropanol-acetone leaching treatment.

This report has shown that even relatively straightforward procedures can produce unexpected results when used without an understanding of their limitations. The limitations of the procedures for the preparation of dry and leached cakes and the subsequent determination of combined water from these cakes have been defined and procedures specified to increase the reliability of the determinations.

REFERENCES

Borisov, V. M., L. G. Berezkina, T. I. D'yakonova, and S. I. Borisova. 1983. Defluorination of phosphogypsum. The Soviet Chemical Industry. 15: 826-829.

Ljunggren, P. 1960. Determination of mineralogical transformations of gypsum by differential thermal analysis. J. Am. Cer. Soc. 43: 227.

Meredith, C. L. 1965. The nature and distribution of fluorine in the hydrochloric acid processing of Florida phosphate pebble. Ph.D. thesis. Louisiana State University.

Savinkova, E. I., V. I. Gashkova, V. N. Desyatnik, and B. A. Popov. 1985. Dehydration of phosphogypsum. The Soviet Chemical Industry. 17: 353-356.

Wiedemann, H. G. and G. Bayer. 1975. Thermal decomposition processes and their nucleation characteristics. Z. Anal. Chem. 276: 21-31.

RECRYSTALLIZATION OF CALCIUM SULFATE MODIFICATIONS IN PHOSPHORIC ACID

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ABSTRACT

Calcium sulfate hemihydrate and dihydrate were batchwise recrystallized into anhydrite in a solution containing 40 w% P_2O_5, 2 to 12 w% H_2SO_4 at temperatures ranging from 70 to 100 °C. Hemihydrate was converted into dihydrate in a solution of 15 to 25 w% P_2O_5 with varying sulfate concentrations at temperatures from 40 to 70 °C. The rate of conversion and the Cd uptake by the formed crystals was determined in dependance of the type and amount of seed crystals and a a function of process conditions such as temperature, sulfate and phosphate concentration in the solution. The rate of both conversions was affected by the amount of seed crystals, while for anhydrite no induction period preceeded the recrystallization when no seed crystals were added. The Cd uptake appeared to be very sensitive to the process conditions and was much higher for anhydrite than for dihydrate. The rate of conversion into dihydrate was retarded by the presence of AlF_3 in the solution and even more by Ce^{3+} ions. Impurities in 'black acid', originating from the ore, hampered the conversion into dihydrate and promoted the Cd uptake in anhydrite. Comparison was made between the Cd uptake during batchwise conversion with the uptake 'obtained by continuous crystallization of dihydrate and anhydrite.

1. INTRODUCTION

Phosphoric acid for application in the fertilizer industry is usually produced via a so called wet process. The overall reaction ruling most wet phosphoric acid processes is the digestion of fluoroapatite ore and the precipitation of calcium sulfate by the addition of sulfuric acid, according to:

$$Ca_{10}(PO_4)_6F_2 + 10\ H_2SO_4 + x\ H_2O \longrightarrow 6\ H_3PO_4 + 10\ CaSO_4.xH_2O + 2\ HF$$

where, depending on the process conditions either dihydrate (x=2), hemihydrate (x=1/2) or anhydrite (x=0) is formed. Which of the three phases is formed, depends on the temperature as well as on the sulfate and phosphate concentration of the crystallizing solution, as will be discussed below. In current processes only DH or HH is precipitated, while formation of AR does not occur in any commercial phosphoric acid process.

During crystallization cadmium ions, originating from the ore, are incorporated in the calcium sulfate lattice due to isomorphous replacement of calcium ions. This happens because the ionic radii of these two ions are almost equal ($r(Cd^{2+})=107$ pm, $r(Ca^{2+})=112$ pm, both for an 8-fold coordination [Huheeh, 19751). Uptake of cadmium in the byproduct is problematic, because the calcium sulfate is usually disposed, and especially in Europe strong regulations are imminent against the disposal of cadmium in river water or even at sea. According to a similar substitution mechanism HPO_4^{2-} ions can replace SO_4^{2-} ions in the crystal lattice. This uptake should also be kept at the lowest possible level, because it reduces the phosphate efficiency of the process. Another unwanted impurity is radium. Radium is coprecipitated with the calcium sulfate due to the very low solubility of radium sulfate. When the calcium sulfate byproduct is used as a building material, the radium content is bound to strict limits. In poorly ventilated rooms radon gas, a decay product of radium, may build up to health-hazardous concentrations.

In order to improve product as well as process characteristics, such as the phosphate uptake and the quality of the crystals, recrystallization of one calcium sulfate phase into another under carefully controlled conditions is often applied in phosphoric acid processes. Examples are hemihydrate-dihydrate processes [3], where initially formed hemihydrate (HH) is transformed to dihydrate (DH). The reverse reaction, the DH to HH recrystallization, is applied in the Prayon process [Becker, 1983].

During the direct crystallization as well as during recrystallization the uptake of cadmium and phosphate are determined by the process conditions and by the nature of the precipitated phase (HH, DH or HH). Process conditions are for instance the P_2O_5 and H_2SO_4 concentration of the solution, the temperature and the production rate. In general minimization of uptake is pursued. There is, however, one example where the purposely incorporation of cadmium in AH, which is at least ten times higher than in HH or DH, has been patented as a method for the production of phosphoric acid with a low cadmium content [Weterings and Janssen, 1986]. In this process cadmium is removed from the recycled phosphoric acid stream by precipitation of a small amount of AH which contains most of the cadmium. The conditions of the AH precipitation depend on the required reduction in cadmium level of the phosphoric acid, but are e.g. 40 % P_2O_5, 10 % H_2SO_4 and a temperature of 95°C.

In order to study the cadmium uptake by AH, recrystallization experiments were performed from DH or HH into AH under different conditions. Because in existing processes the cadmium uptake also becomes increasingly important, such data about the HH into DH recrystallization were also obtained.

More generally defined the objective of this work is to determine the relationship between the uptake of cadmium and phosphate and the nature of the precipitating phase as well as the process conditions. The conversion rate is also an important parameter to be known, not only because it determines the dimensions of the recrystallization equipment, but also because of its influence on the uptake of P_2O_5 and Cd by the crystals through the growth kinetics. The effect of the linear growth rate of calcium sulfate upon the degree of incorporation of foreign ions like Mg^{2+} and Sr^{2+} has already been described in the literature [Kushnir, 1980]. For comparison of the Cd uptake during conversion with the uptake during continuous crystallization, a few DH and AH crystallization experiments were performed under almost identical process conditions.

2. PHASE DIAGRAM AND CONVERSION RATE

As mentioned, important parameters of the (re)crystallization process are the P_2O_5 and H_2SO_4 concentration of the solution and the temperature. In figure 1 the stability of the three phases is indicated as a function of the P_2O_5 content of the solution and the temperature.

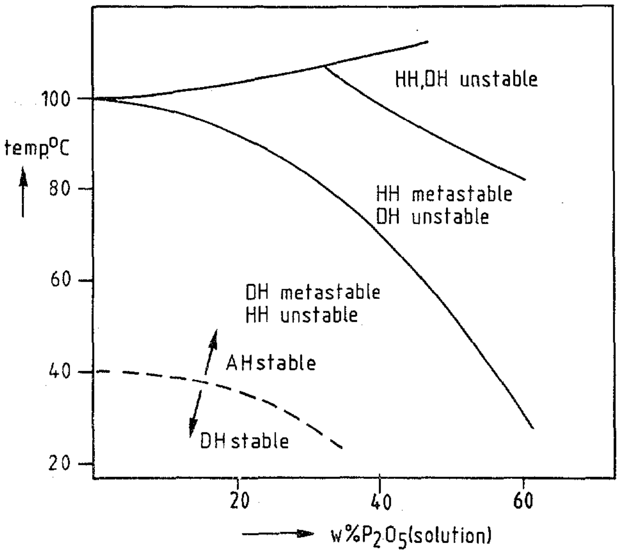

Figure 1.

Stability of the three calcium sulfate phases in phosphoric acid. Note that HH only exists as a metastable phase, and that AH is stable in the largest part of the diagram.

In this diagram the additional presence of H_2SO_4 can be taken into account by taking 1 w% H_2SO_4 equal to about 1 w% P_2O_5. The role of H_2SO_4 and P_2O_5 in the formation of the different phases can be explained by considering the activity of water as the determining factor in the stability of the three phases. The three phases contain different percentages of water, leading to a dependancy of their stability on the activity of water. At higher acid concentrations, the amount of free water, and therefore the activity of water, is lower. This favours formation of a more dehydrated phase, i.e. AH or HH, with respect to a less dehydrated phase, i.e. DH. At higher temperatures, water tends to form looser bonds, in the crystal and also in the solution, thus favouring the vapour phase; the vapour pressure increases. This makes less water containing calcium sulfate modifications more stable at high temperatures. From the diagram AH appears to be stable in the largest part of the diagram, that is above 40°C in pure water, and above lower temperature levels at increasing P_2O_5 concentrations. Up to high temperatures and acid concentrations, however, metastable DH and HH can be formed in the stable AH region. This results from the fact that AH growth proceeds very slowly in a large part of the diagram. Eventually these metastable DH or HH phases will be transformed into AH, but this only occurs with measurable speed at high temperatures and acid concentrations. It can further be seen that HH only exists as a metastable phase. Conversion of HH into DH and vice versa can occur by crossing the DH-HH equilibrium line, i.e. by bringing HH into the metastable DH region, or by bringing DH into a solution which satisfies the metastable HH conditions. Any transition of the three phases into each other is possible, except the AH into HH conversion. This is because HH can only be formed in a region where AH is stable.

In the recrystallization reaction three steps can be distinguished:

i) dissolution of the source material,

ii) diffusion transport through film layers at the surface of the dissolving crystal and at the newly formed phase,

iii) growth of the new phase. In case no or not sufficient seed crystals are present, the growth step is preceeded by a nucleation step.

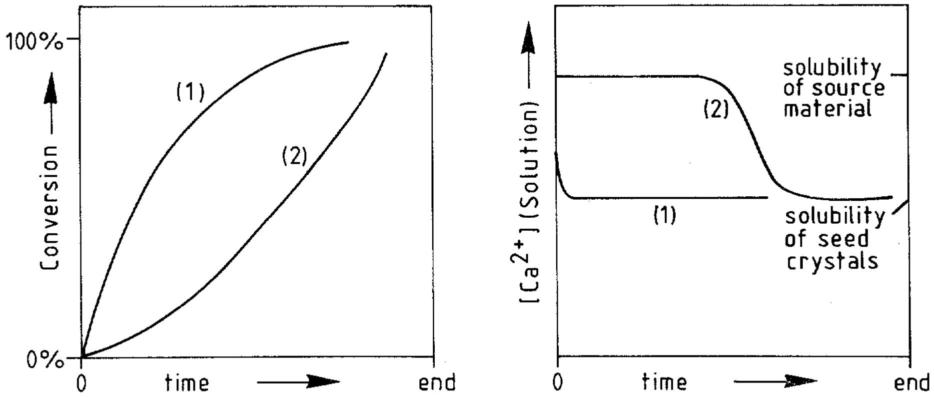

Fig. 2a: degree of conversion and 2b: calcium concentration versus reaction time. Conversion rate controlled by: (1) dissolution of source material or (2) growth of seed crystals

It is important to know which step is rate determining under various conditions, because such knowledge allows the conversion rate to be optimized. The rate determining step (r.d.s.) of the conversion can in principle be derived from the shape of the recrystallization curve obtained from batch experiments [Cardew and Davey, 1985]. This curve is a plot of the percentage conversion versus the reaction time. If the dissolution of the source material is rate determining, the conversion proceeds faster at the start when the amount of source material is the largest. Curve (1) is then obtained, for which the conversion rate, given by the slope of the curve, decreases with time, as shown in figure

2a. If, on the contrary, the growth of the newly formed phase is rate determining, the increasing surface area of the growing crystals will give rise to an increasing conversion rate. The shape of the obtained curve is then given by curve (2). The two curves (1) and (2) represent two extremes, since one step is rate determining while the others proceed infinitely fast. It can, however, as well be assumed that in batch processes the growth is the r.d.s. at the start of the conversion, but that when the conversion is almost completed, the dissolution becomes rate limiting. During most of the conversion the situation is lying somewhere in between, i.e. the conversion rate is determined by both the dissolution of the source material and the growth of the newly formed phase. The obtained conversion curve then lies between (1) and (2), and it is hard to tell only from the shape of the curve to what extent dissolution and growth play a rate determining role.

During the recrystallization of the $CaSO_4$ phases, the rate of dissolution must be lying rather close to the growth rate (both in kg/s), because the low solubility of DH, HH or AH does not allow any significant amount of calcium sulfate material to be stored by and removed from the solution, compared to the total amount of recrystallized calcium sulfate. At H_2SO_4 concentrations of 5 to 10 w% the amount of calcium in the solution can be taken as a measure for the concentration of calcium sulfate in the solution, because the sulfate concentration can be considered constant during the experiment.

During recrystallization the calcium concentration of the solution will decrease in time, from the solubility value of the source material to the solubility of the newly formed phase. Thus, in the same way as the conversion versus time curve, the shape of the calcium concentration versus time curve enables us to derive information about the r.d.s. (see figure 2b). Additional evidence about the r.d.s. can be obtained by varying the relative amounts of seed and source material to see how the conversion rate responds to these variations.

The rate at which a transition takes place depends, as mentioned before, on the growth rate of the newly formed phase and on the rate of dissolution of the source material. Both rates have a driving force which directly depends on the relative supersaturation or undersaturation, i.e. on the differences between the actual $CaSO_4$ concentration and the solubilities of the respective phases. The $CaSO_4$ concentration is normally given in grams per kg solution. Often, however, in the different experiments the molar calcium over sulfate ratio in the solution is not equal to one, but varies from 1 to 1/200, depending on the sulfate concentration in the solution. It is therefore more convenient to use the square root of the product of the calcium and sulfate concentrations as a measure for the solubility and for the actual calcium sulfate concentration. This value equals the concentration of calcium sulfate given in grams/kg solution at stoichiometric calcium and sulfate concentrations. Since the sulfate concentration of the solution is known and remains about constant during the conversion, only the calcium content of the solution has to be measured for the calculation of the newly defined calcium sulfate concentration. The difference between the actual concentration and the solubility value now equals $\sqrt{[Ca]*[H_2SO_4]} - \sqrt{[Ca]eq*[H_2SO_4]eq}$ and the relative supersaturation is given by:

$$\sqrt{([Ca]*[H_2SO_4])} / \sqrt{([Ca]eq*[H_2SO4]eq)} - 1$$

In these formulas the charges of the ions are left out. The growth rate will increase when the supersaturation increases, which happens when the actual concentration is higher. Dissolution on the other hand, occurs faster when the actual calcium sulfate concentration is lower. So a large difference in solubilities of the newly formed phase and the phase of the source material favours a fast conversion. This situation can for the HH into DH or for the reverse recrystallization be reached by selecting the process conditions not too close to the HH-DH equilibrium line. In figure 3 as an example the solubilities of the three $CaSO_4$ phases at 60°C are given as function of the P_2O_5 concentration [Slack, 1968].

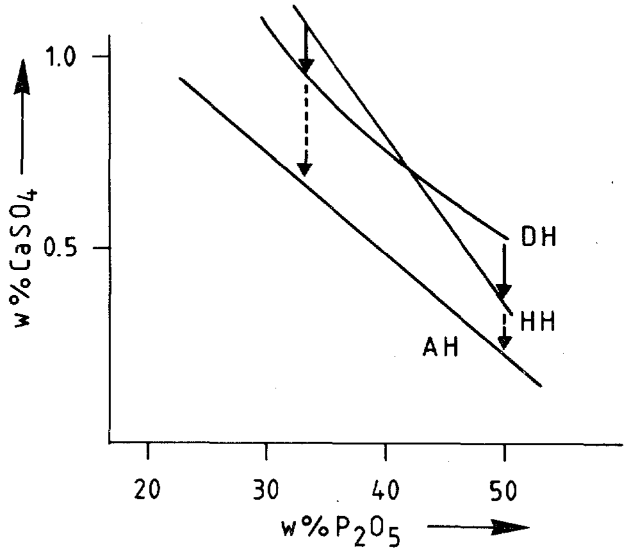

Figure 3.

Solubility of calcium sulfate as a function of the phosphate concentration at 60 °C.

At all phosphate concentrations AH is the most stable phase and has thus the lowest solubility. Below 40 w% P_2O_5 DH is more stable than HH and at further decreasing P_zO_5 concentrations the relative difference in solubilities becomes greater. A low P_2O_5 concentration therefore stimulates the HH into DH conversion. Analogously, it can be derived that high P_2O_5 concentrations stimulate the DH into HH conversion. Also for the HH or DH to AH conversion the relative difference *in* solubility becomes greater which explains why this conversion is also stimulated by high P_2O_5 concentrations. As mentioned above, the influence of H_2SO_4 is the same as of P_2O_5 in the phase diagram, and this is also true for the solubility. H_2SO_4 has, however, not only an effect as an acid, like phosphoric acid, in affecting the solubility of the calcium sulfate, but also as a constituent ion of the calcium sulfate, influencing the molar Ca/SO_4 ratio in the solution. It is known from literature data [Becker, 1983] that sulfate ions at low concentrations up to a few w%, generally enhance the conversion rate of any of these phase transitions. The effect of sulfate ions is therefore not unambiguous.

Next to the P_2O_5 and H_2SO_4 concentration and the temperature, impurities originating from the phosphate ore may influence the solubility or the difference in solubility between two phases. The influence of impurities is therefore not only directly noticeable on the growth kinetics, but also indirectly, via the solubility. For instance, AlF_3 can have considerable influence on solubility of HH and DH in a 35 w% P_2O_5 solution at 95°C. [Glazyrina et al., 1980].

3. EXPERIMENTAL

In all experiments chemically pure $CaSO_4.2H_2O$, H_3PO_4, H_2SO_4, $3CdSO_4.8H_2O$, $Ce(NO_3)_3.6H_2O$ were used. In the experiment with so called "black" acid, phosphoric acid from a Nissan H process was used. In case of the HH into DH conversions the experiments were performed in a thermostated double walled hard glass vessel. The experimental procedure is given schematically in figure 4.

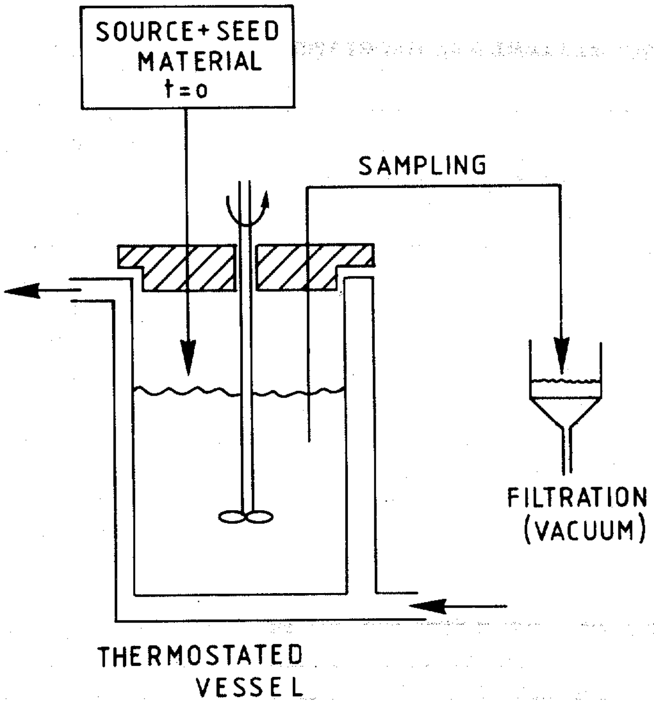

Figure 4.

Setup of the recrystallization experiments.

The vessel was filled with a solution of the selected P_2O_5 and H_2SO_4 concentrations and a Cd^{2+} concentration of 100 ppm. First either AH or DH seed crystals were added, whereafter the experiment was initiated by the addition of DH or HH source material free from or with a known content of cadmium and P_2O_5. During at least one hour samples were taken from the slurry at regular intervals. After filtration of the sample over a G4 filter, the crystals were first washed three times with a hot saturated gypsum solution in water to remove the phosphoric acid, and subsequently three times with acetone to remove the adhering water from the crystals. The filtrate was diluted with water in a sample flask to avoid after-precipitation of the supersaturated solution. For the HH into DH recrystallizations p.a. gypsum from Merck was used as seed material for the first conversion. After this first conversion, the recrystallization was always repeated at least once, where in the second recrystallization the product of the first conversion was used as a seed material. So called α HH, obtained during continuous crystallization (see below) was used as source material. For the conversion of DH or HH into AH the AH seed material was prepared by recrystallizing DH in a Cd-free 40 w%P_2O_5, 10 w% H_2SO_4 containing solution at 90°C. The source material was either a HH obtained from continuous crystallization or ß HH obtained by drying p.a. gypsum (Merck) at 150°C during 24 hours, or the source material was p.a. DH (Merck). For this conversion a slightly modified set-up was used. In order to avoid evaporation of the solution at the necessarily high temperatures, a closed round bottom vessel placed in a thermostated bath was used. For only one of these experiments the conversion was repeated, using the AH from the former conversion as seeds.

A few continuous crystallization experiments were performed. The experimental procedure is described extensively in ref. [Sluis et al., 1986]. In each experiment a solution of Ca^{2+} in phosphoric acid (about 1 mole Ca^{2+}/kg) was added continuously together with concentrated H_2SO_4 to the crystallizer, except for the experiment with 'black acid', where a stream of $Ca(OH)_2$ slurry in water was added simultaneously with a stream of 'black acid', containing 20 w% H_2SO_4. The slurry volume in the reactor is kept constant by continuous, unclassified removal of slurry from the crystallizer. The residence time of the slurry, defined as the reactor volume divided by the slurry volume stream, was varied from 20 to 60 minutes. In each experiment a steady state was obtained after 8 residence times. The solid over liquid weight ratio was about 11 %. Samples were taken each residence time, and treated similarly as for the batch experiments. For the production of AH temperatures of 90 to 100°C were maintained in a solution of 40 w% P_2O_5 and 5 to 10 w% H_2SO_4, while the DH production took place at 60°C in a solution of 25 w% P_2O_5 and 1 to 10 w% H_2SO_4.

The Ca and Cd contents of the solution as well as the P_2O_5 and Cd contents of the crystals were measured by means of inductive coupled plasma spectroscopy (ICP). The crystals were dissolved in HCl and then diluted to about 1 gram calcium sulfate per 100 ml solution. Corrections were made for the initial impurity contents of the seed crystals. The H_2O content of HH/DH samples was determined by placing the samples overnight in an exsiccator dried over silicagel, followed by weighing and then by glowing at 800°C for two hours, and weighing again. In this way a reproducable value of about 6 w% H_2O for the otherwise varying water content of HH (0.1 - 7 w%) could be obtained.

4. RESULTS AND DISCUSSION

4.1. RECRYSTALLIZATION OF HEMIHYDRATE AND DIHYDRATE INTO ANHYDRITE.

4.1.1. Conversion curves and expressions for Cd uptake.

The conditions at which the conversion takes place, are determined by the region of the phase diagram, where both DH and HH are unstable or where metastable HH rapidly transforms into AH. For most of the conversions into AH conditions were selected of 90°C, 40 w% P_2O_5 and H_2SO_4 concentrations above 5 w%. Some experiments were performed at slightly different conditions of temperature, w% P_2O_5 and w% H_2SO_4. The amount of AH formed per kg solution was kept low in accordance with the patented process [Weterings and Janssen, 1986], mentioned in the introduction. Only 2 to 5 w% AH was formed in the solution of 40 w% P_2O_5 and 10 w% H_2SO_4 at 90°C. The amount of added AH seed material varied from 0 to 10 %. All results are given in table 1. $\tau(50\%)$ indicates the time required for 50 % conversion. In this table also results of the continuous crystallization experiments are given. As an example, the results of an experiment with 2 w% AH seeds will be discussed, where α HH was used as a source material (exp. 3). In figure 5 the resulting Cd and Ca concentrations of the solution are plotted versus the reaction time.

Table 1. HH and DH into AH recrystallization

		solution						crystals		
exp. nr.	conversion	$\%P_2O_5$	$\%H_2SO_4$	ppm Ca	%seeds	%source	T(°C)	K(Cd)	D(Cd) (10^{-3})	$\tau(50\%)$ (min)
1	αHH→AH	40	10	200	0	2	90	40	27	5
2	αHH→AH	40	10	195	1	2	90	60	40	4
3	αHH→AH	40	10	180	2	2	90	62	40	3.5
4	αHH→AH	40	10	160	5	2	90	48	26	3
5	αHH→AH	40	10	145	10	2	90	39	19	1.5
6	αHH→AH	40	5	475	1	5	90	18	29	
7	βHH→AH	40	5	215	1	5	80	27	20	17
8	βHH→AH	40	5	425	1	5	90	18	26	12
9	βHH→AH	40	5	375	1	5	100	27	28	5
10	DH→AH	40	5	320	1	5	100	22	24	12
11	AH cont	40	10	140	10%solids		90	38	18	(chem. pure)
12	AH cont	40	11	170	10%solids		90	65	38	(black acid)
13	DH→AH	35	12		5	5	90	23		
14	DH→AH	45	12		5	5	90	79		

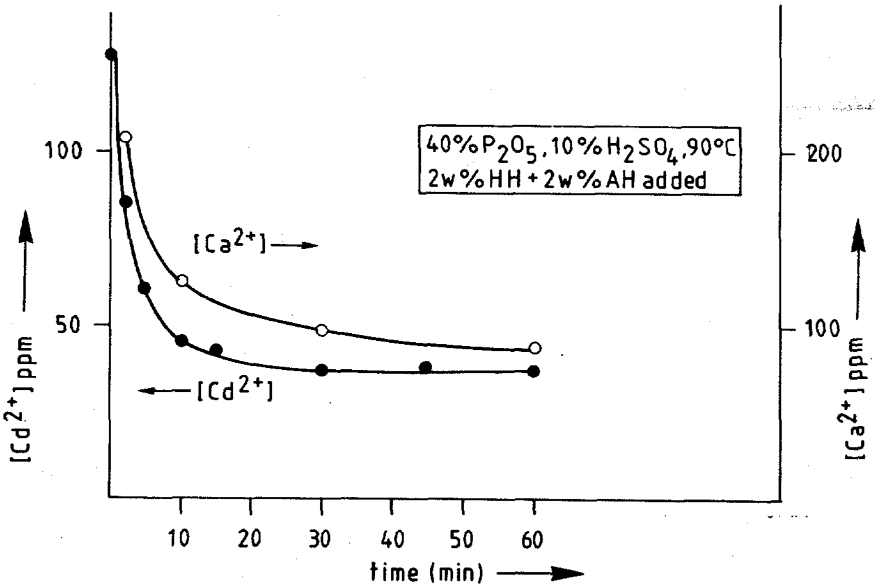

Figure 5.

Cd and Ca concentration in the solution during the recrystallization of αHH into AH.

The Cd concentration decreases as a result of the high Cd incorporation in the newly formed AH. When the Cd concentration remains constant, the conversion is assumed to be completed. The still continuing slight decrease in Ca concentration can be calculated to contribute negligibly to the AH mass or to the conversion. It follows from figure 5 that the main part of the conversion is completed within 10 minutes. In this period the Ca concentration decreases from about 200 ppm at 2 minutes reaction time to 120 ppm. Comparison with figure 2b shows that the shape of-the curve during this period is lying between curve 1 and 2. This implies that the conversion is at least to some extent controlled by the dissolution of the α **HH** crystals. This also follows from the shape of the conversion curves presented in figure 7 (section 4.1.2.). This result is probably related with the quality of the α HH crystals, which are prepared by continuous crystallization. These crystals are rather large with a length of up to 1000 µm and dissolve rather slowly due to their low specific surface area. In another experiment (exp. 8), where 5 w% ß HH was added to a 40 w% P_2O_5 solution with 5 w% H_2SO_4 and 1 w% AH, the Ca versus time curve remains more or less constant at a high level of about 400 ppm during most of the conversion period (see figure 6). The ß HH used here consists of aggregates of tiny crystals with a high specific surface area. These crystals dissolve easily and the Ca versus time curve resembles curve 2 in figure 2b, where the conversion is growth determined. The higher Ca levels of this curve result from the lower H_2SO_4 concentration in solution. The control by growth also follows from the shape of the conversion curves in figure 11 (section 4.1.4.). For the DH into AH conversion, where fine grained DH from Merck was used, similarly shaped Ca and Cd versus time curves were obtained as for the ß HH into AH conversion. The DH into AH conversion process, however, proceeded significantly slower. This is also illustrated by comparing the two conversion curves at 100°C in figure 11, which will be discussed in section 4.1.4. (exp.9, 10)

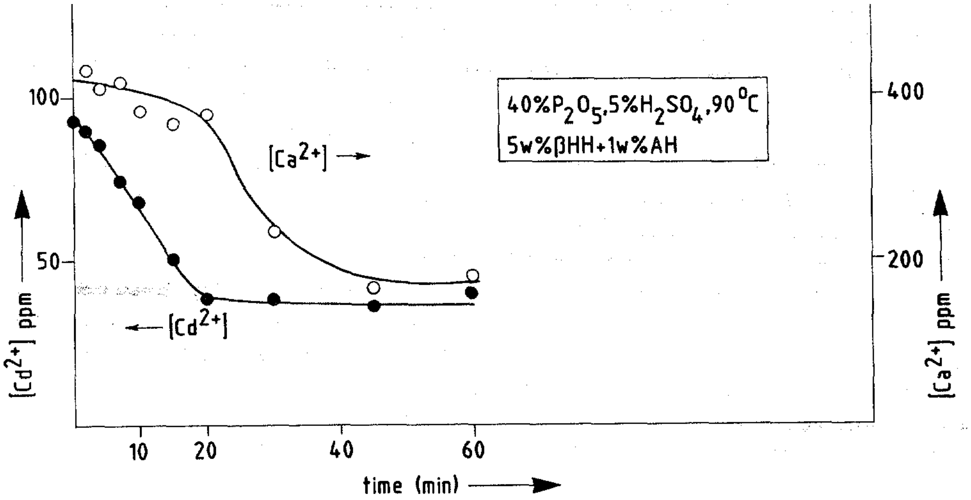

Figure 6. Cd and Ca concentration in the solution during the recrystallization of ß HH into AH.

In order to express the degree of conversion in a quantitative way several techniques are available. The simplest way, however, is to use the Cd concentration in solution as a measure. This method is feasible, since the Cd uptake in AH is high. The degree of conversion at time t can be calculated from the remaining Cd concentration at the given time, combined with the Cd concentrations at the start and at the end of the conversion. This leads to the following expression for the degree of conversion:

conversion (t) = mass of formed AH (t) / mass of formed AH (end)

$$= \frac{\ln\left([Cd](0)/[Cd](t)\right)}{\ln\left([Cd](0)/[Cd](end)\right)} \qquad (1)$$

The derivation of this equation is *given in* the appendix. The Cd uptake can be expressed by a distribution coefficient K(Cd), given by:

$$K(Cd) = [Cd]\ (crystal)/[Cd](solution) \qquad (2)$$

or by a partition coefficient D(Cd):

$$D(Cd) = [Cd]/[Ca]\ (crystal)\ /\ [Cd]/[Ca]\ (solution) \qquad (3)$$

Because in the batch experiments the Ca and Cd concentrations are not constant in time, K(Cd) and D(Cd) must be obtained by integration. The derivation is given in the appendix. K(Cd) is more for practical use, because this is the parameter that is directly measured , while D(Cd) gives a better description of the cadmium incorporation since e.g.

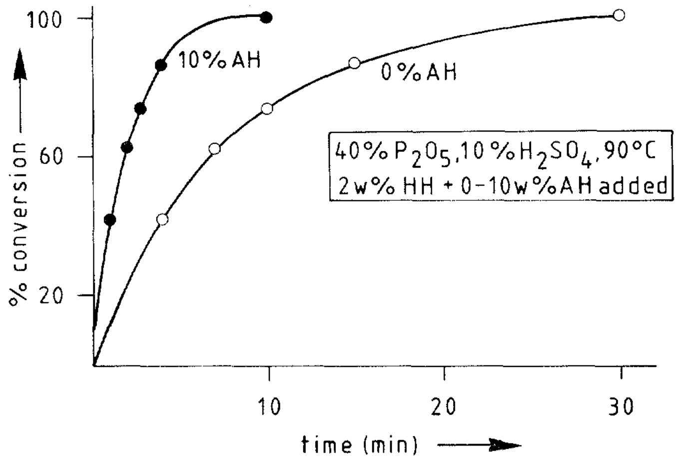

Figure 7.

Influence of the amount of AH seed crystals on the conversion of αHH into AH.

The addition of seed crystals gives rise to a higher conversion rate, as follows from the steeper slope of the curve. The conversion rate thus seems to be more governed by the precipitation rate of the AH than by the dissolution rate of the HH crystals. The role of the amount of seed crystals is even more obvious, if the conversion rate instead of the percentage conversion is taken. The conversion rate is expressed as the inverse of time needed to reach a certain percentage of conversion. In figure 8 the so defined conversion rate is plotted versus the percentage of AH seeds, For each percentage conversion the obtained curve is almost a straight line, which means that the conversion rate is directly proportional to the amount of AH seed crystals. This indicates that the growth of the AH rules the process. Since the shape of the conversion

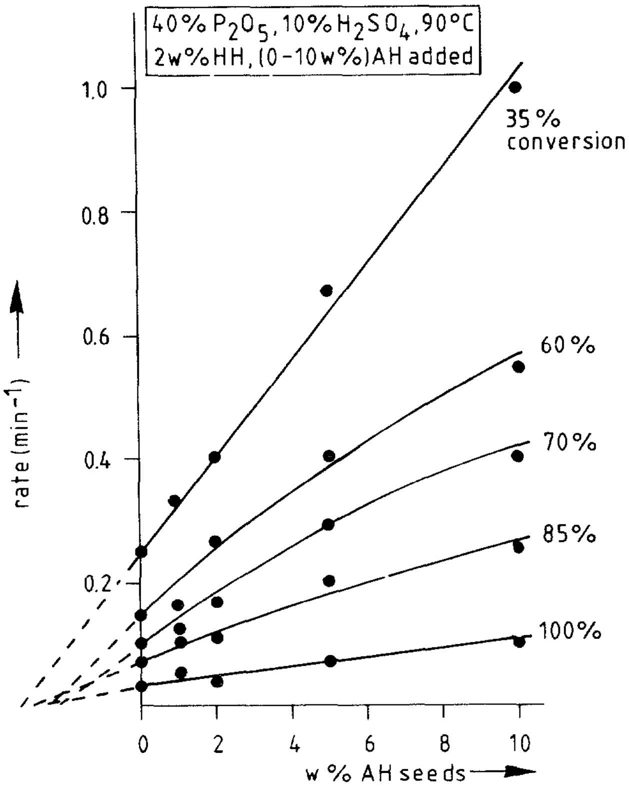

Figure 8.

Conversion rate of αHH into AH as a function of the amount of AH seed crystal.

curve for a HH into AH rather resembles a conversion curve of a process dominated by the dissolution of the source material than one dominated by the growth of the newly formed phase, the shape of a conversion curve alone is not conclusive except perhaps for the two extreme cases (see section 4.1.1.). The conversion rate is not zero when no seed crystals are added, but a value of the intercept of -2 w% AH is found in figure 8. Heterogeneous nucleation of AH upon the HH crystals may explain this phenomenon. The high temperature and acid concentration needed for AH growth might promote heterogeneous nucleation of AH, since under more moderate conditions AH nucleates slowly.

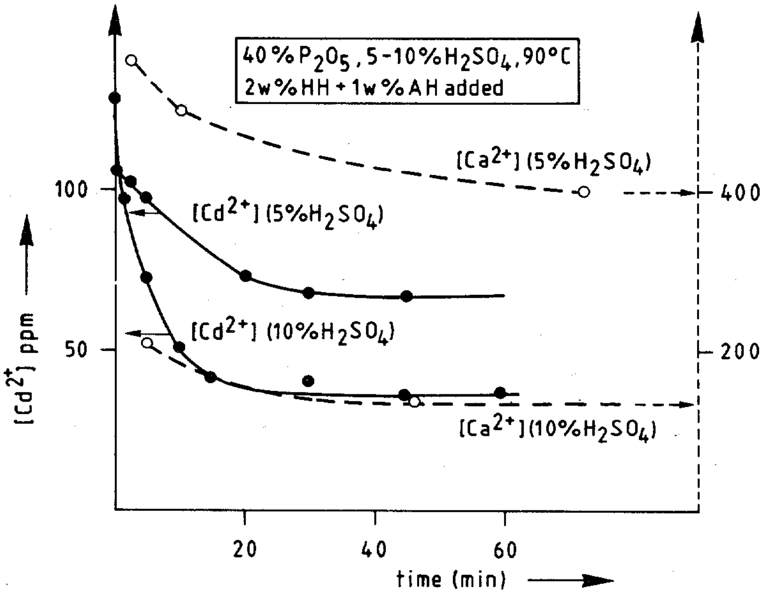

Figure 9.

Influence of the H_2SO_4 concentration in the solution on the Cd and Ca concentration during αHH into AH recrystallization.

4.1.3. Influence of the H_2SO_4 content.

The influence of the H_2SO_4 content of the solution was studied by performing experiments with different H_2SO_4 concentrations under further identical conditions of 40 w% P_2O_5, 90°C, 2 w% a HH and 1 w% AH (exp. 2,6 6). In figure 9 the Cd and Ca concentration are plotted as a function of time, for 5 and 10 w% H_2SO_4 in the solution respectively. For 5 w % H_2SO_4 , total conversion was achieved in about 30 minutes, while for 10 % a reaction time of 20 minutes was required. Sulfate ions thus stimulate the conversion. For a 5 % H_2SO_4 solution the Ca concentration remains much higher than for 10 % (about 400 and 150 ppm respectively). The Ca concentration is directly related to the sulfate content via a solubility product of $CaSO_4$. It can also be seen in the figure that for 10 % H_2SO_4 the Cd concentration remaining in the solution is lower (30 % of the original content vs. 70 % for 5 % H_2SO_4), and thus the Cd uptake in the formed AH higher. The K(Cd) can be calculated to be about 18 for 5 % H_2SO_4 in the solution, while for 10 % H_2SO_4 a value of 60 is obtained. The corresponding D-values are $3*10^{-2}$ and $4*10^{-2}$.

The influence of the sulfate concentration on the Cd uptake by the AH crystals is elucidated by plotting K(Cd) versus the sulfate concentration (figure 10). It can be seen that K(Cd) increases from about 2 at 2 w% H_2SO_4 to about 50 at 10 %. The spread in data at 10 %, K(Cd) ranges from 40 to 65, in dependence on the amount of seed material used is significant. This spread is probably caused by the lower supersaturation when larger amounts of seed crystals are used. The DH. into AH recrystallization experiments showed about equal K(Cd) values during conversion as for the HH into AH conversions at corresponding H_2SO_4 concentrations. Comparison of 3 K(Cd) value of about 40, and a D of $1.8*10^{-2}$, obtained from continuous (MSMPR) crystallization experiments of AH with these data shows a good agreement (exp. 11). When in these continuous crystallization experiment so called 'black acid' is used (exp. 12), K(Cd) is 65 (D = $3.8*10^{-2}$). This higher uptake with respect to the experiment in chemically pure acid is caused by the impurities in the solution. An explanation for this phenomenon has yet to be found.

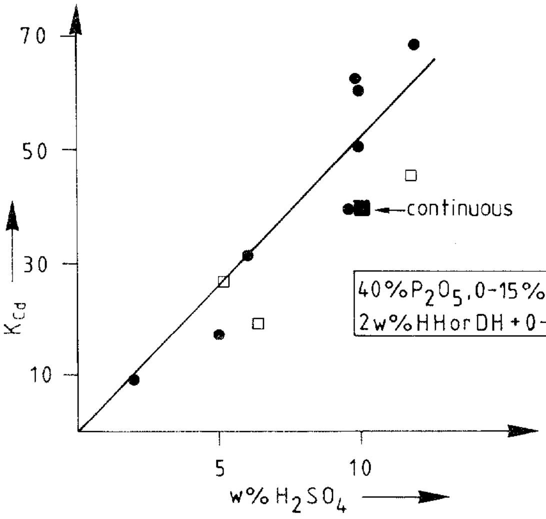

Figure 10.

K(Cd) versus the H_2SO_4 concentration in the solution. Comparison with continuous crystallization ■ and with DH into AH conversion (□).

From the D(Cd) values for AH, as summarised in table 1, it follows that the value of D(Cd) is lying between 2 and 4 * 10^{-2}. Other experiments, not presented here, show that this D-value is constant for up to 20% replacement of Ca^{2+} ions in the AH structure by Cd^{2+} ions. Variations in D(Cd) can, as mentioned, be related to differences in growth rate. The lowest D value can be expected at equilibrium conditions, where the growth rate is zero. During growth the Cd^{2+} ions at the crystal surface can be entrapped by propagating growth layers. At higher growth rates, i.e. at higher supersaturations, the uptake will thus increase. A constant D value at a given growth rate implies that the Cd uptake is directly proportional to the ratio of the Cd and Ca concentrations in the solution. This means that the Cd uptake is determined by a competition between the Cd and Ca ions in solution and thus by their relative rate of impingement upon the crystal surface. If the Ca concentration decreases, K(Cd) is favoured in the competition and the uptake, reflected by K(Cd), will increase. This can be achieved by e.g. a higher sulfate concentration in the solution or by a decrease in $CaSO_4$ solubility.

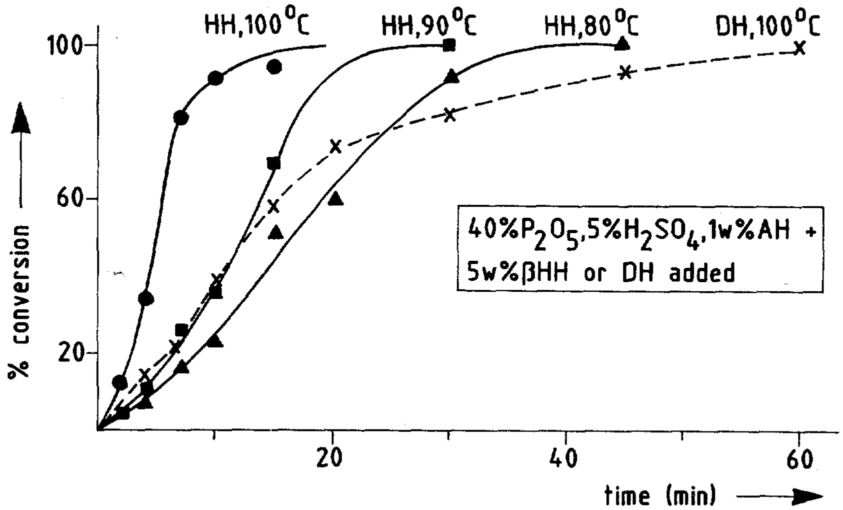

Figure 11. Conversion of βHH and DH into AH at various temperatures.

4.1.4. Influence of the temperature.

To study the influence of the temperature upon the HH into AH conversion, additional experiments were performed at 80 and 100°C in 40 w% P_2O_5, 5% H_2SO_4 with 5 w% ß HH and 1 w% AH seed crystals (exp. 7 to 9). The calculated percentage conversion was plotted as a function of time in figure 11. In particular the hollow shape curve below 50% conversion points at a growth dominated conversion process, as follows from comparison with curve 2 in figure 2a. The last parts of the conversion curves, obtained when the conversion is almost completed, indicate a dissolution controlled process as can be expected. The conversion rate, given by the shape of the curve demonstrates a higher conversion rate at increasing temperature. Comparison of the ß HH into AH with the DH into AH conversion curve (exp. 10), both at 100°C, show that the latter proceeds more than two times slower. Surprisingly no lower D(Cd) value was found. More evidence is needed here. The D(Cd) values for the ß HH conversion are increasing with temperature, which can be related to the higher growth rates at elevated temperatures. In experiments, described by [Witkamp et al., 1986] the P_2O_5 uptake in AH, formed in 40 w% P_2O_5 and 12 % H_2SO_4 is low and decreases from 0.25 % at 70°C to 0.14 % at 90°C. This decrease at higher growth rate must be resulting from another effect, which compensates for the higher uptake expected at higher growth rates.

4.1.5. Influence of the P_2O_5 concentration

To explore the influence of the P_2O_5 concentration upon the Cd uptake a few additional experiments were done on the α HH into AH conversion in a 35 and 45 w% P_2O_5, 10 % H_2SO_4 solution at 90°C with 5 w% HH and 5 w% AH. The K(Cd) values given in tabel 1 (exp 13,14) reveal a strong increase in uptake at higher P_2O_5 concentrations. This increase is probably caused by a decrease in $CaSO_4$ solubility, but for these experiments not enough data of the Ca concentration were available to calculate D.

4.2. RECRYSTALLIZATION OF HEMIHYDRATE INTO DIHYDRATE.

4.2.1. Influence of the seeds

The conditions where HH transforms into DH follow from the region of the phase diagram, where HH is unstable and DH stable or metastable. The conversions were carried out in solutions with 15-25 w% P_2O_5, 0-12 w% H_2SO_4, 10-16 w% α HH and 5-8 w% DH. The influences of the amount of seeds, the H_2SO_4 and P_2O_5 concentrations of the solution as well as the temperature upon the conversion rate have not been studied systematically, since these effects are already extensively described. [Taperova (1950), Slack (1968) and Becker (1983)]. Only a few selected experiments were performed.

Contrary to the HH into AH recrystallization it appeared to be necessary to perform each conversion a second time, using the obtained DH from the first conversion as seed material for a second. This second conversion always proceeds at least 10 % slower. Performing the conversion a third time hardly has any influence on the conversion rate. A very small effect of repeated conversions can be expected, because the crystals become slightly larger after each conversion. The specific surface area of the DH thus decreases, giving rise to a lower conversion rate, if the reaction is growth rate controlled, because the amount of added seed crystals is constant. The necessity of a second conversion can be owed to the use of p.a. gypsum (Merck) as seed material for the first conversion, while for the AH experiments the seeds were prepared in phosphoric acid and resembled therefore more those formed at the selected recrystallization conditions. All results given in table 2 refer to the second conversion. τ(50%) denotes the time required for 50 % conversion. In the table also the results of continuous crystallization experiments at 20 and 60 minutes residence time are given (τ20 and τ60).

Table 2. HH and DH into AH recrystallization

exp. nr.	con- version	solution						crystals			
		%P_2O_5	%H_2SO_4	ppm Ca	%seeds	%source	T(°C)	%P_2O_5	K(Cd)	D(Cd) (10^{-3})	τ(50%) (min)
15	αHH→DH	25	6		0	10	65				50
16	αHH→DH	25	6		5	10	65				7
17	αHH→DH	>15	0.6	2600	5	10	40	1.4	0.20	2.2	
18	αHH→DH	15	2	1500	5	10	40	1.0	0.20	1.3	
19	αHH→DH	15	5	900	5	10	40	0.7	0.25	1.0	
20	αHH→DH	15	10	600	5	10	40	0.7	0.31	0.8	
21	αHH→DH	15	0.7	3000	5	10	60	1.1	0.20	2.5	
22	αHH→DH	15	2	1600	5	10	60	0.9	0.27	1.9	
23	αHH→DH	15	5	1100	5	10	60	0.6	0.31	1.5	
24	αHH→DH	15	10	900	5	10	60	0.4	0.43	1.6	
25	DH	25	1	3000	10		60	1.6	0.14	2.0	(cont. cryst. τ20)
26	DH	25	6	730	10		60	0.65	0.43	1.5	(cont. cryst. τ20)
27	DH	25	11	470	10		60	0.47	0.85	1.7	(cont. cryst. τ20)
28	DH	25	5	900	10		60	0.35	0.28	1.1	(cont. cryst. τ60)
29	αHH→DH	25	6		9	16	50	0.44	0.42		10
30	αHH→DH	25	6		9	16	60	0.32	0.43		16
31	αHH→DH	25	6		9	16	70	0.25	0.37		60
32	αHH→DH	15	6		9	16	60	0.37	0.37		7.5
33	αHH→DH	20	6		9	16	60	0.38	0.38		5
34	αHH→DH	25	6		9	16	60	0.42	0.43		60
35	αHH→DH	15	10		9	16	70	0.30	0.60		8
36	αHH→DH	15	10		9	16	70	0.32	0.60		27 (black acid)
37	αHH→DH	25	6		5	10	70				35
38	αHH→DH	25	6		5	10	70				60 (0.8 %AlF_3)
39	αHH→DH	15	10		9	16	70	0.39	0.48		9 (10 ppm Ce^{3}+)
40	αHH→DH	15	10		9	16	70	0.33	0.65		17 (20 ppm Ce^{3}+)
41	αHH→DH	15	10		9	16	70	0.38	0.49		68 (100 ppm Ce^{3}+)
42	αHH→DH	15	10		9	16	70	0.39	0.59		140 (250 ppm Ce^{3}+)

Apart from the influence of the type of seed crystals on the conversion rate, also the effect of the amount of seeds was tested. In figure 12 the percentage conversion is plotted versus the reaction time for an experiment with no seeds added and for an experiment with 5 w% DH seeds under further identical conditions (exp. 15, 16). The shape of the curve obtained with seeding resembles the a HH into AH conversion curve given in figure 7. This conversion is thus at least to some extent controlled by the dissolution of a HH. When no seeds are added an induction period of about 30 minutes preceeds the development of DH. At the given relatively mild conditions needed for DH growth the a HH crystals do not seem to act as heterogeneous nuclei for DH.

For these experiments the Ca and Cd concentrations were not determined as a function of time during conversion, but only at the start and at the end. The mean Ca concentrations of the two samples presented in table 2 are taken as representative for the Ca concentration during the conversion. Since the Cd uptake by DH appeared to be much lower than for AH, the decrease in Cd concentration in the solution could neither be used for the calculation of K(Cd) nor for the determination of the degree of conversion. For this reason the K(Cd) was directly derived from the analyzed Cd incorporation in the DH crystals. The degree of conversion could accurately be deduced from the crystal water content of the sample.

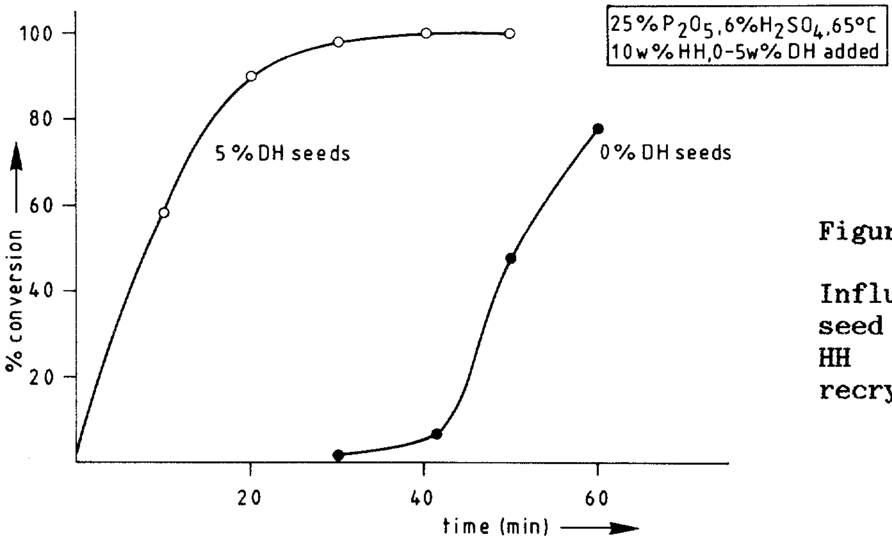

Figure 12.

Influence of amount of seed material on the HH into DH recrystallization.

4.2.2. Influence of the H_2SO_4 concentration

The influence of the H_2SO_4 concentration in the solution was tested by recrystallizing 9 w% HH with 6 w% DH seeds in 15 w% P_2O_5 at 40 and 60 ^{0}C (exp. 17 to 24). The lowest H_2SO_4 concentration was calculated from the stoichiometric calcium concentration, because no H_2SO_4 was added. When the H_2SO_4 concentration increases from 0.6 % to 10 %, K(Cd) increases slightly from 0.20 to 0.31 at 40 ^{0}C, and from 0.20 to 0.43 at 60 ^{0}C. This minor increase is in contrast with the increase in K(Cd) for AD from about 5 to 50 in this range. The increase is very small since the Ca concentration decreases far less at higher H_2SO_4 concentrations here than for the DH into AH conversion. At the relatively low P_2O_5; concentration used here for the HH into DH conversion, the solubility of calcium sulfate is enhanced by an increase in H_2SO_4 concentration, as can be seen from the [Ca]*[H_2SO_4] product which can be calculated from table 2. This higher solubility compensates for the decrease in calcium concentration at higher H_2SO_4 concentrations due to the constancy of the solubility product. Since variations in the Ca concentration are taken into account in the calculation of D(Cd), its value should be constant. Table 2, however, shows that D(Cd) is not constant but decreases at both 40 and 60 °C with higher H_2SO_4 concentrations. These decreases in D(Cd) may be caused by the use of an average of two values of the calcium concentration instead of the measured actual Ca concentrations, and have to be verified by measuring the actual Ca concentration during the conversion as has been done for the conversions into AH. The D-value of 1.7*10-3 at 60 °C corresponds with D values obtained for continuous crystallization experiments of DH in 25 % P_2O_5 at 60 °C, at H_2SO_4 concentrations between 1 and 10 % (exp. 25 to 27). The residence time in these experiments was 20 minutes. When instead of 20 minutes 60 minutes was taken, the D-value diminished to $1.1*10^{-3}$ (exp. 28). This indicates that the supersaturation and thus the growth rate, being higher for a shorter residence time, plays a role in the uptake. The observed D(Cd) value for DH of about 1 to $2*10^{-3}$ is remarkably lower than for AH. The difference by a factor of about 20 can not be caused only by a difference in growth rate or by the different process conditions, but is probably inherent to the different calcium sulfate phases.

The P_2O_5 uptake by the DH phase during recrystallization decreases with the H_2SO_4 content of the solution, as shown in table 2. In analogy with the Cd/Ca competition in solution determining the Cd uptake, the phosphate over sulfate ratio is expected to dominate the phosphate uptake. This has formerly been proved to be true for the phosphate uptake by HH in 40 w% P_2O_5 [Sluis et al. , 1986). For these HH into DH recrystallization experiments, however, such a competition model apparently does not describe the yielded P_2O_5 values in DH, presented in table 2. An explanation for this discrepancy might be a change in the constituents of the solution in the 15 to 25 % P_2O_5 concentration range. According to Elmore (1965) the composition of the solution changes in this range from mainly H_2PO_4- and H_3PO_4 constituents into $H_5P_2O_8-$ ions. In our case, in a 15 w% P_2O_5 solution the effect of an increasing amount of H_2SO_4 could be comparable with that of P_2O_5. This change in composition of the solution might affect the phosphate uptake by the crystals.

4.2.3. Influence of the temperature

Comparison of the Cd and P_2O_5 uptake results obtained for experiments performed at 40 and at 60 °C, shows an increase in K(Cd) and D(Cd), and a decrease in the P_2O_5 uptake at increasing temperature. Additional experiments, however, performed at 50, 60 and 70 °C in a 25 w% P_2O_5 and 6 w% H_2SO_4 containing solution (exp.29 to 31), gave rise to about equal K(Cd) values, which are also about equal to those obtained for the former experiments with 5 to 10 % H_2SO_4. No final conclusions can therefore so far be drawn about the influence of the temperature on the Cd uptake, only that this effect will be small. The decreasing P_2O_5 uptake at higher temperatures is more obvious. This tendency is consistent with the results found for AH. To quantify the conversion rate at the various temperatures only the times required to achieve a 50 % conversion are presented. These times increase from 10 minutes at 50 °C through 16 minutes at 60 °C to 60 minutes at 70 °C. This tendency can be ascribed to the smaller difference in solubility between the HH and DH phases at higher temperatures, causing a lower driving force for the conversion.

4.2.4. Influence of the P_2O_5 concentration

The influence of the P_2O_5 concentration on the Cd and P_2O_5 uptake in DH was studied by performing experiments at 60 ° in solutions containing 15, 20 and 25 w% P_2O_5 and 6 w% H_2SO_4. The effect of the variations in P_2O_5 concentrations upon the Cd and P_2O_5 uptake is only minor, as can be seen in table 2, exp 32 to 34. The time, needed to reach 50 % conversion , however, increases noticeably from about 6 minutes at 15 and 20 w% P_2O_5 to 16 minutes at 25 w% P_2O_5. This can be explained by a smaller difference in solubility between HH and DH at the higher P_2O_5 concentration.

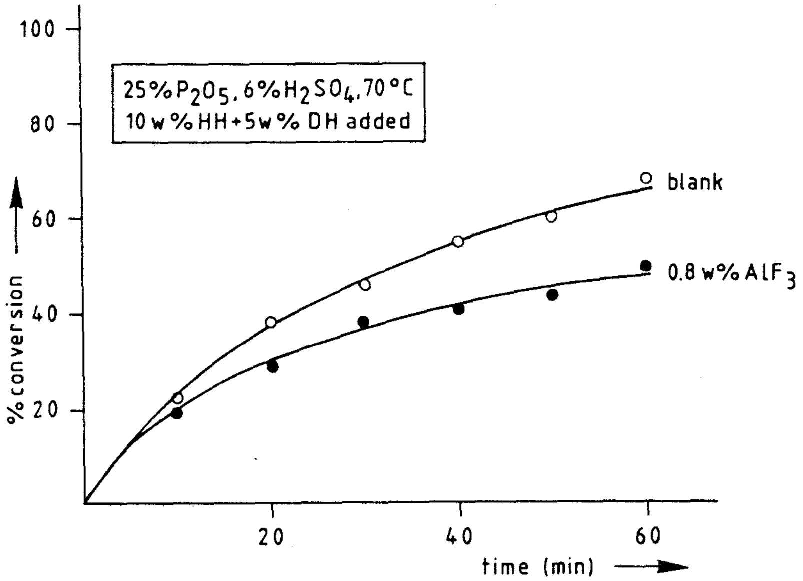

Figure 13.

Influence of AlF_3 on the recrystallization of HH into DH.

4.2.5. Influence of impurities

Next to the already mentioned parameters, the conversion rate strongly depends on the presence of a number of impurities in the solution. One of the impurities, of which the strong impact is well known, is aluminum fluoride. The influence of 0.8 % AlF_3 on the conversion is shown in figure 13, where the conversion is plotted versus the time, with and without AlF_3 in a solution of 25 w% P205, 6 w% H2S04 at 70 °C, and where 10 w% HH and 5 w% DH were added (exp. 37, 38). The conversion rate, given by the slope of the curve, is evidently lower, i.e. about 30 %, in the presence of AlF_3.

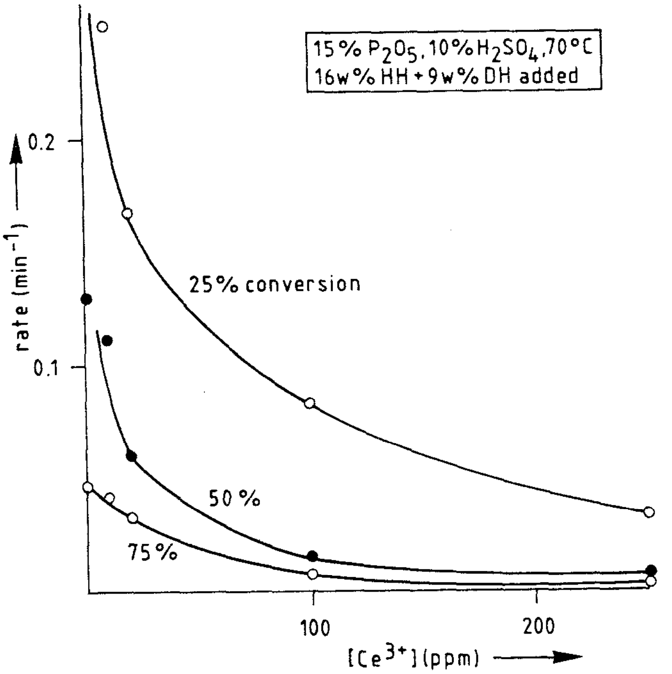

Figure 14.

Rate of conversion of HH into DH as a function of the cerium concentration in the solution.

Other impurities are the lanthanides, which can be present in the phosphate ore in concentrations up to 1 % Ln_2O_3 [Kijkowska, 1983]. The most predominant ion of these is Ce^3+. The influence of Ce^3+ on the conversion rate is even greater. Therefore similar experiments were performed for various Ce^3+ concentrations. (exp. 39 to 42). The results are presented in figure 14. Here the conversion rate is plotted against the Ce^3+ concentration up to 250 ppm of Ce^3+. The conversion rate is expressed as the inverse of the time to achieve 25, 50 and 75 % conversion. Already at 20 ppm Ce^3+ an effect is visible, and at 250 ppm Ce^3+ the conversion rate is decreased by about a factor ten. The concentrations used are much lower than those of AlF_3, and it can be concluded that Ce^3+ is a much stronger conversion inhibitor. Experiments under carefully controlled conditions, where in a 0.1 M $NaClO_4$ solution DH seed crystals were allowed to grow at a constant supersaturation indicate that the Ce^3+ ions affect the growth rate of the DH.

When instead of chemically pure phosphoric acid, acid from a Nissan H proces was used, only the conversion rate was affected. In 15 w% P_2O_5, 10 w% H_2SO_4 at 70 °C the K(Cd) equals in both cases 0.60, and the P_2O_5 uptake is about 0.31 %. (exp. 35, 36). The required time for 50 % conversion increases from 8 minutes in chemically pure acid to 27 minutes in product acid. This decrease in conversion rate is probably imposed by impurities present in the black acid. The concentrations of only the Ce^3+ and AlF_3 ions in the solution are, however, not high enough to be responsible for this decrease in conversion rate. The Ce^3+ concentration was estimated to be 10 ppm, while the AlF_3 concentration was a few tenth %.

5. CONCLUSIONS

From the results the following conclusions can be drawn:

1. The recrystallization of HH or DH into AH in batchexperiments can easily be followed by recording the Cd content of the solution, because the uptake of Cd in AH is very high. The rate of conversion is determined by the growth of AH, but can also to some extend be affected by the dissolution of the source material.
2. Under the given conditions, where conversion of HH into AH is completed within an hour, no induction period is observed. The addition of seed crystals, however, strongly promotes the conversion.
3. Under conditions where the recrystallization of HH into DH is completed within half an hour, an induction period of half an hour preceeds the conversion when no seeds are added. The conversion rate depends on by the type of seed crystals used.
4. Conversion into AH proceeds faster at higher H_2SO_4 and P_2O_5 concentrations. The Cd uptake by AH is also higher under these conditions.
5. The Cd uptake in AH and DH can be described by a competition between Cd and Ca ions, and will thus be low at high Ca concentration in the solution.
6. The P_2O_5 uptake in DH and AH on the contrary, is lower at higher H_2SO_4 concentrations and temperatures. The P_2O_5 concentration in the solution plays a less important role.
7. The uptake of Cd in DH and AH can be expressed by a partition coefficient D, which equals 2 to $4*10^{-2}$ for AH and 1 to $2*10^{-3}$ for DH. The obtained D-value depends slightly on the supersaturation, through the growth rate of the crystals.
8. The conversion of HH into DH is stimulated by low temperatures and low P_2O_5 concentrations. Literature data have shown that the H_2SO_4 concentration causes an optimum in the conversion rate. The Cd uptake increases slightly with increasing H_2SO_4 concentrations, and with increasing temperatures. The P_2O_5 concentration has no visible effect.
9. Impurities can have strong influence on the conversion rate as has been shown for the HH into DH transformation. AlF_3 retards the conversion, and $Ce^{3}+$ has this effect even more. Conversion in black acid, containing a number of impurities, proceeds considerably slower than in chemically pure acid. The presence of these impurities promotes the Cd uptake during continuous crystallization of AH.

6. ACKNOWLEDGEMENT

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7. REFERENCES.

Becker, P. 1983, Phosphates and phosphoric acid. Fertilizer Science and Technology Series, Vol.3. Dekker, New York.

Bevington, P.R. 1969. Data reduction and error analysis, McGraw-Hill, New York.

Cardew, P.T. and R.J. Davey. 1985. The kinetics of solvent-mediated phase transformations. Proc. R. Soc. Lond. 398 415-428

Elmore, K.L. et al. 1965. J. Phys. Chem. 69 3520.

Glazyrina, L.N., et al. 1980. Solubility of calcium hemihydrate and dihydrate in phosphoric acid containing $A1^{3+}$, F^- and SiF_5^{2-} ions. Translated from Z. Prikladnoi Khimii, 53 2524-2527.

Huheey, J.E. 1975. Inorganic-Chemistry. Harper and Row, New York.

Kijkowska, R. 1983. Recovering rare earth elements from Kola apatite and Moroccan phosphate rock. Phosphorus & Potassium 127 24

Kushnir, J. 1980. The coprecipitation of strontium, magnesium, sodium, potassium and chloride ions with gypsum. An experimental study. Geochim. et Cosmochim. Acta 44 1471.

Slack, V.. 1968, Phosphoric Acid. Fertilizer Science and Technology Series, Vol.1. Dekker, New York.

Sluis et al. 1986. Crystallization of calcium sulfate in concentrated phosphoric acid. J. Crystal Growth 79 (1986) 620-629

Taperova, A.A; and M.N. Shulgina. 1950.. The kinetics of the transformation of the crystal hydrates of calcium sulfate in the presence of phosphoric acid J. Appl. Chem (USSR) 23 27

Weterings, C.A.M, and J.A. Janssen. July 1986. Patent pending. (nr. 8601846 Dutch Patent Office).

Witkamp, G.J S.P.J. Schuit and G.M. van Rosmalen. 1986. Recrystallization of calcium sulfate modifications in phosphoric acid. Condensed papers of the Second International Congress on phosphogypsum, Miami 1986, University of Miami.

8. APPENDIX: CALCULATION OF CADMIUM UPTAKE AND CONVERSION

8.1. DISTRIBUTION COEFFICIENT K(Cd)

The dimensionless distribution coefficient K(Cd) is defined as the ratio of the Cd concentration in the crystals and in the solution:

$$K(Cd) = [Cd^{2}+](crystals)/[Cd^{2}+](solution).$$

For continuous crystallization experiments, where a steady state can be obtained, the steady state values of the concentrations were used to calculate K(Cd). For batch experiments, however, the Cd concentration in the solution is not constant, but decreases with time due to the uptake of cadmium by the newly formed calcium sulfate crystals. Under the assumption that K(Cd) is constant during the experiment, K(Cd) can be calculated by integration.

The Cd uptake in kg (d Cd) per kg formed $CaSO_4$ is given by:

$$d\,Cd / d\,CaSO_4 = [Cd^{2}+](solution)*K(Cd) \iff$$

$$d\,Cd = [Cd^{2}+](solution)*K(Cd)*d\ CaSO_4$$

Dividing both sides by the total amount of solution gives:

$$d[Cd^{2}+](solution) = -\ [Cd^{2}+](solution)*K(Cd)*d[CaSO_4]$$

The minus sign develops because the amount of Cd taken up by the calcium sulfate has been replaced by the amount of being removed from the solution. Sorting out parameters and integration leads to:

$$\int_{begin}^{end} \frac{d[Cd^{2}+](solution)}{[Cd^{2}+](solution)} = -\ K(Cd)* \int_{begin}^{end} d[CaSO_4] \iff$$

$$\ln \frac{[Cd^{2}+](begin)}{[Cd^{2}+](end)} = -\ K(Cd)*([CaSO_4](end) - [CaSO_4](begin)) \iff$$

$$K(Cd) = \frac{1}{[CaSO_4](formed,end)} * \ln \frac{[Cd^{2}+](begin)}{[Cd^{2}+](end)},\ [CaSO_4] \text{ in kg/kg} \quad (1)$$

8.2. PARTITION COEFFICIENT D

For the Cd-$CaSO_4$ system the partition coefficient D is defined as the molar ratio $Cd^{2}+/Ca^{2}+$ in the formed crystals divided by the same ratio in the solution:

$$D = \frac{[Cd^{2}+]/[Ca^{2}+](crystals)}{[Cd^{2}+]/[Ca^{2}+](solution)} \quad (1)$$

In the following the charges of the ions will be omitted.

In the continuous crystallization experiments, D is obtained by inserting the steady state concentrations of Cd and Ca in Eq. 1. In batch experiments, however, the Cd and Ca concentrations are a function of the reaction time. Under the assumption that D is constant during the experiment, D can be calculated from the Cd and Ca concentrations in the solution as a function of time, and the total amounts of solution and formed crystals.

The reaction time is divided in fractions Δt, and starts at t = 0. During the interval At the Cd concentration in the-solution changes:

$\Delta[Cd](solution) = [Cd](t+\Delta t) - [Cd](t)$

The Ca concentration in this interval has the mean value [Ca](t). The Cd concentration in the $CaSO_4$ formed during the time interval Δt; denoted as $\Delta CaSO_4$, is given by:

$$[Cd](\Delta CaSO_4) = -\ \Delta[Cd](solution)*\frac{\text{mass of the solution}}{\text{mass of formed } CaSO_4} \qquad (2)$$

From the definition of D (equation 1) and from the relation

[Ca](crystal) = 1/0.136 (mole/kg) for anhydrite it follows that:

$$[Cd](\Delta CaSO_4) = \frac{D*[Cd](solution)}{0.136*[Ca](solution)} \qquad (3)$$

Combining equations 2 and 3 gives:

$$\Delta CaSO_4 = -\frac{\Delta[Cd](solution)*0.136*[Ca](solution)*\text{mass of solution}}{D*[Cd](solution)} \qquad (4)$$

(4) can be summated to yield the total amount of formed $CaSO_4$:

$CaSO_4$ (totally formed) =

$$-\sum_{i=1}^{i=n} \frac{([Cd](i\tau/n) - [Cd]((i-1)\tau/n))*0.136*[Ca](i\tau/n)*\text{mass of solution}}{D * [Cd](i\tau/n)} \qquad (5)-$$

where all concentration refer to concentrations in the solution; τ denotes the total reaction time. The summation can be written as an integral for n approaching infinity:

$$\frac{\text{totally formed } CaSO_4}{\text{mass of solution}} = -\int_{0}^{t(end)} \frac{(d[Cd](t)/dt) * 0.136 * [Ca](t)}{[Cd](t) * D}\, dt \qquad (6)$$

Since D and the left hand side of (6) are constant in time, they may be exchanged without affecting the result of the integration:

$$D = -\int_{0}^{t(end)} \frac{(d[Cd](t)/dt) * 0.136 * [Ca](t)}{[Cd](t) * (\text{totally formed } CaSO_4/\text{mass of solution})} dt \qquad (7)$$

(7) can be evaluated when the Cd and Ca concentrations are known as a function of time. In order to allow this calculation, both concentrations are fitted by a function

$$g(t) = a_1 + a_2 * \sqrt{t} + a_3 * t + a_4 * (t+1)^{1/4} + a_5 * (t+1)^{-1/2} + a_6 * \exp(t/10) \qquad (8)$$

For each set of data a_1-a_6 are calculated, yielding a best fit. For the fitting procedure an algorithm of Marquard is used [Bevington,1965] in a Pascal program. This algorithm also allows optimization of functions not linear in its parameters. The program runs with Turbo Pascal (Borland Inc.) on a MS-DOS compatible personal computer. Concentrations are expressed in ppm and the reaction time in minutes. For instance, for the data of exp. 3, the following functions are obtained for t = 0 to t = 25 minutes:

$$[Cd](\text{solution}) = 250.059 + 46.3767 * \sqrt{t} + 2.54038 * t - 220.1932 * (t+1)^{1/4} + 100.590 * (t+1)^{-1/2} - 2.47568 * \exp(t/10); \qquad (9)$$

$$[Ca](\text{solution}) = 922.223 + 43.9845 * \sqrt{t} + 12.5996 * t - 556.221 * (t+1)^{1/4} - 109.487 * (t+1)^{-1/2} - 6.63790 * \exp(t/10) \qquad (10)$$

From Eq. 9 it follows directly that

$$\frac{d[Cd](t)}{dt} = 23.188 * t^{-1/2} + 2.54038 - 55.0483 * (t+1)^{-3/4} - 50.2952 * (t+1)^{-3/2} - 0.247568 * \exp(t/10) \qquad (11)$$

From Eq. 7, 9, 10, 11 and the conversion

[Ca] (mole/kg) = (Ca] (ppm)*$2.5*10^{-5}$ an expression for D follows, after a new fitting procedure

$$D = -\int_{0}^{t(end)} \left(1.72977*10^{-2} - 2.042173*10^{-2}*\sqrt{t} + 1.102350*10^{-3}*t + 4.50295*10^{-2}*(t+1)^{+1/4} - 3.67131*10^{-2}*(t+1)^{-1/2} - 2.56303*10^{-4}*\exp(t/10) \right) dt \qquad (12)$$

, yielding D = 0.040 for this example.

8.3. THE CONVERSION.

8.3.1. Calculation from the Cd concentration in the solution.

This method is only applicable to the conversion of HH or DH into AH.

The conversion at time t is defined by:

$$\text{Conversion}(t) = \frac{\text{mass of formed } CaSO_4(t)}{\text{mass of formed } CaSO_4(\text{end})} \qquad (1)$$

Under the assumption that K(Cd) remains constant during the recrystallization, the degree of conversion at time t can be calculated from Eq. 1, section 8.1.

$$K(Cd) = \frac{1}{[CaSO_4](\text{formed},t)} * \ln \frac{[Cd](\text{begin})}{[Cd](t)} \qquad (2)$$

from Eq. 1 and 2 follows that

$$\text{conversion } (t) = \frac{[CaSO_4](\text{formed},t)}{[CaSO_4](\text{formed},\text{end})} = \frac{\ln(\ [Cd](\text{begin})/[Cd](t))}{\ln(\ [Cd](\text{begin})/[Cd](\text{end}))} \quad (3)$$

8.3.2. Calculation from the Cd and Ca concentration in the solution.

(Only for the HH or DH conversion into AH)

The conversion as defined as in section 8.3.1., Eq. 1, yields, combined with Eq. 6, section 8.2., on integration to t instead of to t(end):

$$\text{conversion}(t) = \frac{1}{[CaSO_4](\text{end})} * = \int_{0}^{t} \frac{(d[Cd](t)/dt\ \ * 0.136 * [Ca](t)}{D * [Cd](t)}\, dt$$

8.3.3. Calculation of the conversion from the crystal water content.

This method is only worked out for the HH into DH conversion.

Assume that at the start is present an amount of dihydrate DH(0) and hemihydrate HH(0). The masses at time t are denoted as DH(t) and HD(t). The solubility of calcium sulfate is neglected. The conversion is defined as :

$$\text{conversion}(t) = \frac{\text{DH}(t)-\text{DH}(0)}{\text{DH(end)}} \qquad (1)$$

Pure dihydrate contains 20.9 w% H_2O, and hemihydrate contains 6.2 %. The crystal water content of the sample, taken at time t contains x % H_2O. The fraction of dihydrate in the sample is then give by Eq. 2:

$$\text{fraction dihydrate}(t) = \frac{x(t)-6.2}{14.7} \qquad (2)$$

Since the molar weight of dihydrate is 172, and of hemihydrate is 145 grams/mole, the total crystal mass increases during the conversion:

$$\begin{aligned} \text{mass}(t) &= \text{DH}(t) + \text{HH}(t) \\ &= \text{DH}(0) + \text{conversion}(t)*\text{HH}(0)*\frac{172}{145} + (1-\text{conversion}(t))*\text{HH}(0) \\ &= \text{DH}(0) + \text{HH}(0)*(\frac{27}{145}*\text{conversion}(t)+1) \qquad (3) \end{aligned}$$

The fraction dihydrate is also equal to DH(t)/mass(t). This gives, in combination with Eq. 2 and 3:

$$\frac{x(t)-6.2}{14.7} = \frac{\text{DH}(0) + \text{conversion}(t) * \text{HH}(0) * (172/145)}{\text{DH}(0) + \text{HH}(0) * (27/145 * \text{conversion}(t)+1)} \qquad (4)$$

yielding, after rearrangement of parameters:

$$\text{conversion}(t) = \frac{14.7 * \text{DH}(0) + (6.2-x(t)) * (\text{DH}(0) + \text{HH}(0))}{\text{HH}(0) * (x(t) * 27/145 -18.59)} \qquad (5)$$

THEHMOCHEMICAL EVALUATION OF CALCIUM SULFATE DECOMPOSITION REACTIONS

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ABSTRACT

The thermochemistry of $CaSO_4$ is of technical interest in two important areas. The first area is the reductive decomposition of calcium sulfate (phosphogypsum or natural gypsum) for production of two desirable products: sulfur or sulfuric acid and cement. The second area is for the regeneration of undesirable sulfate waste products from flue--gas desulfurization processes using limestone to abate SO_2. Many previous studies of the thermochemical behavior of $CaSO_4$ were carried out for process development purposes; how--*ever,* there is no comprehensive compilation of thermochemical data for $CaSO_4$. Therefore, a JANAF-type thermodynamic data sheet for $CaSO_4$ was developed. Using these data and existing thermodynamic data for SO_2, CaO, CO, and CO_2, the probable reaction routes involving $CaSO_4$ formation and decomposition under different reaction conditions (temperature and pressure) were evaluated. The effect of other reactants, such as oxidizing or reducing agents, on the decomposition of the calcium sulfate also was postulated.

The thermodynamic evaluation indicates that a potential new reaction route to produce elemental sulfur from calcium sulfate under reducing conditions may be a cost-effective method, compared to the known technology of SO_2 formation and subsequent sulfuric acid production.

INTRODUCTION

Regeneration or recycling of waste calcium sulfate to the valuable raw materials has been studied extensively by many organizations; however, there are no clear--cut answers because of the many options and complexities of the process. Calcium sulfate has been generated mainly from the phosphate industry as a by-product (Slack, 1968), but an additional source from the power industry is emerging as a new potential environmental challenge (Shepard, 1985). These two calcium sulfates are quite different in physical and chemical properties, but both contain calcium sulfate as the main component. Therefore, regeneration reaction mechanisms and kinetics may be applied for both by-products. Thermal regeneration processes of calcium sulfate to produce sulfuric acid have been studied for 60 years (Duda, 1966; Foerster and Kubel, 1924; Hull et al., 1957; Lloyd et al., 1985; Swift and Wheelock, 1975; Swift et al., 1976; Wheelock, 1958; Wheelock and Boylan, 1960), and the process has been proved to be technically feasible. A few plants were built (Hull et al., 1957) and operated in Europe, but no commercial-size plant has been built in the United States. Whenever the sulfur price soared to a peak in the business cycle, a few new research activities to recover sulfur from calcium sulfate were initiated. However, the process was not accepted as a viable alternative to the sulfur-burning sulfuric acid process. A recent development of the atmospheric fluidized bed combustion (AFBC) technique to abate air pollution from coal-fired power plants is expected to generate huge quantities of waste calcium sulfate by-product (Skopp et al., 1969; Smith, 1985; Vogel et al., 1973).

Recent cost estimates by the Tennessee Valley Authority (TVA) (Salladay et al., 1986) indicated that thermal regeneration of AFBC waste to sulfuric acid and portland cement is an economically attractive alternative, compared to the separate plant operation of sulfuric acid and cement. The sulfuric acid which may be produced from the thermal decomposition reaction of calcium sulfate is used for further production of phosphoric acid or used as a raw material for other chemical processes, However, the logistics of sulfuric acid transportation or supply/demand equations may hamper those sulfuric acid producers who have no captive facilities for the acid. On the other hand, elemental sulfur is a well-known raw material and can be stored easily; it also can be transported economically in bulk. If a process to produce elemental sulfur instead of sulfuric acid from calcium sulfate is developed, it would be beneficial for the by-product calcium sulfate-producing industry.

Biswas et al. (1971) and others (Turkdogan and Vinters, 1976; Zadick et al., 1972) reported that calcium sulfate was successfully converted to calcium sulfide under reducing conditions. Curran et al. (1973) and Farooqui et al. (1961) investigated the conversion of calcium sulfide to hydrogen sulfide and found the reaction to be a favorable step. The conversion of hydrogen sulfide to elemental sulfur is well known (Pearson, 1973) and has been commercially employed in the energy industry. However, the three--step conversion process to elemental sulfur from calcium sulfate through calcium sulfide and hydrogen sulfide may be a probable process, but may not be economically feasible because of the numerous steps and the high capital investment.

On the other hand, if a one-step conversion process from calcium sulfate to sulfur is developed, it may have great potential for the regeneration of $CaSO_4$. Pechkovskii and Mel'tseva (1964) and Ginstling and Volkov (1960) postulated that elemental sulfur may be formed from calcium sulfate with carbon, but they had no experimental data to back up their claim. Fleck (1952) extrapolated the possibility of a one--step conversion of calcium sulfate to elemental sulfur based on Zawadzki's (1932) and Schenck and Jordan's (1929, 1933) data. Fleck (1952) confirmed the formation of elemental sulfur in his subsequent laboratory test. Recent U.S. patents by Lind (1973) and Gorin (1973) confirmed that elemental sulfur can be produced by a one--step reduction calcination reaction with CO_2 (Lind) or a two-stage conversion reaction (Gorin). These laboratory evidences of sulfur production prompted us to review and evaluate all calcium sulfate decomposition reactions under reducing conditions.

DEVELOPMENT OF THERMOCHEMICAL DATA FOR $CaSO_4$

Many previous studies of the thermochemical behavior of $CaSO_4$ were carried out for process development purposes; however, there is no comprehensive compilation of thermochemical data for $CaSO_4$, which is essential for prediction of the probable reaction routes involving $CaSO_4$ decomposition. Therefore, it was important to develop a JANAF-type (Stull and Prophet, 1971) thermodynamic data sheet for $CaSO_4$. Using these data the probable reaction routes involving $CaSO_4$ formation and decomposition under different reaction conditions (temperature and pressure) can be postulated since the thermodynamic data for SO_2, CaO, and oxygen are already available. The effect of other reactants such as oxidizing or reducing agents on the decomposition of $CaSO_4$ also can be predicted, provided that their thermodynamic properties are known.

The heat of formation and Gibb's free energy for $CaSO_4$ at 298.15°K are available in a recent NBS publication (Wagman et al., 1982). These values are: $\Delta H_f^o = -342.760$ kcal/mol and $\Delta F_f^o = -315.920$ kcal/mol.

The heat capacity (C_p, Cal/mol) for $CaSO_4$ at different temperatures was calculated from the following equation:

$$C_p = A + BT + CT^2 - D/T^2 \qquad (1)$$

where $\underline{T}$ is the absolute temperature, °K; and $\underline{A}$, $\underline{B}$, $\underline{C}$, and $\underline{D}$ are 17.22, 0.02337, 0, and 32560, respectively, as reported by Lowell and Schwitzgebel (1969).

The entropy ($S°$, cal/mol-deg) for $CaSO_4$ was evaluated by the following standard equation:

$$S_T° = S_{298.15}° + \int_{298.15}^{T}(C_p/T)dT + \Sigma Q_r/T_r \qquad (2)$$

or

$$S_T° = S_{298.15}° + [A \ln T + BT + D/2T^2]_{298.15}^{T} + \Sigma Q_r/T_r \qquad (3)$$

where S_T^o and $S_{298.15°}$ are the entropy of $CaSO_4$ at temperature, T, and 298.15^{0}K, respectively; A, B, and D are the same constants as in equation 1; Q_r is the heat of transition that occurs in the temperature range 298.15~T; and T_r is the transition temperature. The specific value for $S_{298.15°}$ is 25.502 (Wagman et al., 1982) and Q_r = 6689.2 cal/mol at 1397^{0}C (Lowell and Schwitzgebel, 1969).

The heat contents, $H° - H_{298.15}°$ (kcal/mol), at different temperatures were calculated from the following equation:

$$H° - H_{298.15}° = \int_{298.15}^{T}(C_p)dT \qquad (4)$$

or

$$H° - H_{298.15}° = [AT + (B/2)T^2 + D/T]_{298.15}^{T} \qquad (5)$$

The heat of formation of $CaSO_4$ at different temperatures was calculated from the following equation:

$$(\Delta H_f°)_T = (\Delta H_f°)_{298.15} + \Delta(H_T° - H_{298.15}°) + \Sigma Q_r \qquad (6)$$

or

$$\begin{aligned}(\Delta H_f°)_T = {} & [(\Delta H_f°)_{CaSO_4} - (\Delta H_f°)_{Ca} - (\Delta H_f°)_{S} - 2(\Delta H_f°)_{O_2}]_{298.15} + \\ & [(H_T° - H_{298.15}°)_{CaSO_4} - (H_T° - H_{298.15}°)_{Ca} - (H_T° - H_{298.15}°)_{S} - \\ & 2(H_T° - H_{298.15}°)_{O_2}] + \Sigma Q_r \end{aligned} \qquad (7)$$

where $(\Delta H_f^\circ)_{Ca} = (\Delta H_f^\circ)_S = (\Delta H_f^\circ)_{O_2} = 0$ because the heat of formation at the reference state is zero.

Finally, the Gibb's free energy, ΔF_f°, for $CaSO_4$ was calculated by the following relationship:

$$(\Delta F_f^\circ)_T = (\Delta H_f^\circ)_T - T\Delta S^\circ \qquad (8)$$

or

$$(\Delta F_f^\circ)_T = [(\Delta H_f^\circ)_{CaSO_4} - (\Delta H_f^\circ)_{Ca} - (\Delta H_f^\circ)_S - 2(\Delta H_f^\circ)_{O_2}]_T$$
$$T(\Delta S^\circ_{CaSO_4} - \Delta S^\circ_{Ca} - \Delta S^\circ_S - 2\Delta S^\circ_{O_2}]_T \qquad (9)$$

where the entropy values for Ca, S, and O_2 are obtained from JANAF tables (Stull and Prophet, 1971).

In addition, log K_p was obtained from the following relationship:

$$\log K_p = -\Delta F_f^\circ/2.303RT \qquad (10)$$

where K_p is the equilibrium constant for the formation of $CaSO_4$ from the elements in their reference states and R is the gas constant, 1.987 cal/mol-deg. The calculated thermodynamic data for $CaSO_4$ are given in Table I.

As indicated in Table I, the formation of $CaSO_4$ from its constituent elements is a quite favorable reaction step, which is demonstrated by the large positive K_p value. Therefore, the decomposition of $CaSO_4$, the opposite reaction step of the formation, will be a difficult reaction to achieve and will require reaction temperatures in the range of 1200°C. It has been demonstrated that the decomposition reaction is promoted by the presence of reducing agents, and the decomposition temperature may be lowered by addition of fluxing agents such as Fe_2O_3. Since carbon and

TABLE I

Thermodynamic Data for $CaSO_4$ (Anhydrite)[a,b]

Temp, °K	C_p, cal•mol^{-1}	S°, cal•mol^{-1} deg^{-1}	H° − H_{298}°, kcal•mol^{-1} deg^{-1}	kcal•mol^{-1}		
				ΔH_f°	ΔF_f°	Log K_p
0	0.000	0.000	-6.282	-342.467	-342.467	–
100	16.301	3.505	-4.118	-342.089	-333.480	728.759
200	21.080	16.557	-2.208	-342.506	-324.697	354.782
298	23.818	25.502	0.000	-342.760	-315.910	231.665
300	23.869	25.650	0.044	-342.764	-315.730	229.990
400	26.365	32.861	2.557	-343.408	-306.676	167.546
500	28.775	39.004	5.314	-343.698	-297.458	130.008
600	31.152	44.461	8.311	-343.718	-288.202	104.969
700	33.513	49.440	11.544	-343.494	-278.965	87.089
800	35.865	54.069	15.013	-356.374	-270.945	74.013
900	38.212	58.429	18.717	-355.589	-260.311	63.207
1000	40.557	62.576	22.655	-354.654	-249.773	54.583
1100	42.900	66.552	26.828	-353.564	-239.336	47.548
1200	45.241	70.385	31.235	-354.096	-228.853	41.676
1300	47.582	74.099	35.877	-352.341	-218.487	36.728
1400	49.921	77.710	40.752	-350.372	-208.261	32.508
1500	52.21	81.234	45.861	-348.185	-198.187	28.873
1600	54.599	84.682	51.204	-345.782	-188.265	25.714
1700	56.938	92.008	56.781	-336.469	-178.515	22.948
1800	59.276	95.329	62.591	-370.522	-168.625	20.472
1900	61.614	98.596	68.636	-367.239	-157.496	18.115
2000	63.952	101.816	74.914	-363.737	-146.549	16.013

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[a] Data are compatible with format employed by JANAF thermochemical tables (op. cit.). Hence, reference states for sulfur are: 0°-368.54°K, crystal, rhombic; 368.54°-388.36°K, crystal, monoclinic; 388.36°-717.75°K, liquid; and 717.75°-2000°K, ideal gas, diatomic S_2. Reference states for calcium are: 0°-721°K, crystal, alpha; 721°-1112°K, crystal, beta; 1112°-1767.4°K, liquid; and 1767.4°-2000°K, ideal monoatomic gas.

[b] Crystalline transition of $CaSO_4$ to new reference state occurs at 1670°K, as indicated by dashed horizontal line.

methane gas are economical and readily available reducing agents, we have examined all probable reactions and intermediate steps which are related to the decomposition of $CaSO_4$ by these reducing agents. The heat of reaction ($\Delta H°$), Gibb's free energy ($\Delta F°$), and equilibrium constant (K_p) for each reaction step at the temperature range 298°-1500°K were calculated from Table I and JANAF tables (Stull and Prophet, 1971) and summarized in Table II. The following relationships were used for the calculations:

$$(\Delta H°)_T = [\Sigma(\Delta H_f°)_{product} - \Sigma(\Delta H_f°)_{reactant}]_T \quad (11)$$

$$(\Delta F°)_T = [\Sigma(\Delta F_f°)_{product} - \Sigma(\Delta F_f°)_{reactant}]_T \quad (12)$$

$$\log K_p = -(\Delta F°)_T/2.303RT \quad (13)$$

$$K_p = P_C{}^c \cdot P_D{}^d / P_A{}^a \cdot P_B{}^b \text{ for } aA + bB \leftrightarrow cC + dD \quad (14)$$

where P is the partial pressure, atm, of each component.

At an elevated temperature, carbon reacts with water to produce CO, H_2, and CO_2 (water--gas reaction):

$$C + H_2O \rightarrow CO + H_2 \quad (15)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (16)$$

The first step (equation 15) is a favorable reaction at or above 1100°K since K_p, is large ($K_p = P_{CO}P_{H2}/P_CP_{H20}$ >10). However, one must realize that the equilibrium state may differ from the instantaneous state of reaction because the reaction may need time to reach the equilibrium state. Some reactions require more time than others, depending on the kinetic parameters and reaction mechanisms. Nevertheless, we can use the K_p value as a guide to predict whether a reaction is favorable since every reaction eventually will reach the equilibrium state, but K_p does not predict a kinetic parameter.

TABLE II

Thermodynamic Data for SO_2 Reduction Reactions

Function	Temp, °K	SO_2	CO	CO_2	COS	H_2S	H_2O, g	CS_2	CH_4	SO_3	CaO	$CaSO_4$	CaS	Eq 15	Log K_{15}	Eq 16	Log K_{16}	Eq 17	Log K_{17}	Eq 18	Log K_{18}	Eq 18-2	Log K_{18-2}	Eq 19
ΔH (kcal• mol^{-1})	298	-70.947	-26.471	-94.054	-33.080	-4.900	-57.798	27.950	-17.895	-94.590	-151.790	-342.760	-113.100	31.327		-9.785		120.023		93.552		111.557		72.996
	400	-71.764	-26.318	-94.070	-33.735	-5.867	-58.042	26.646	-18.636	-95.463	-151.714	-343.408	-113.682	31.724		-9.710		119.930		93.612		112.740		72.895
	500	-72.356	-26.298	-94.091	-34.223	-6.635	-58.277	25.673	-19.316	-96.052	-151.581	-343.698	-114.075	31.979		-9.516		119.761		93.463		113.223		72.716
	600	-72.824	-26.332	-94.124	-34.638	-7.282	-58.500	24.862	-19.916	-96.481	-151.420	-343.718	-114.362	32.168		-9.292		119.474		93.142		113.302		72.412
	700	-73.206	-26.409	-94.169	-35.003	-7.832	-58.710	24.163	-20.429	-96.801	-151.242	-343.494	-114.573	32.301		-9.050		119.046		92.637		113.025		71.962
	800	-86.593	-26.514	-94.218	-48.397	-21.368	-58.905	-2.586	-20.857	-110.111	-151.391	-356.374	-128.067	32.391		-8.799		118.390		91.876		125.441		71.261
	900	-86.577	-26.637	-94.270	-48.407	-21.480	-59.084	-2.563	-21.207	-110.009	-151.389	-355.589	-128.085	32.447		-8.549		117.623		90.986		124.289		70.488
	1000	-86.553	-26.771	-94.321	-48.418	-21.564	-59.246	-2.543	-21.482	-109.891	-151.431	-354.654	-128.147	32.475		-8.304		116.670		89.899		122.910		69.510
	1100	-86.524	-26.914	-94.371	-48.430	-21.621	-59.391	-2.527	-21.696	-109.763	-151.517	-353.564	-128.253	32.477		-8.066		115.523		88.609		121.305		68.338
	1200	-86.490	-27.062	-94.419	-48.442	-21.657	-59.519	-2.512	-21.854	-109.626	-153.429	-354.096	-130.186	32.457		-7.838		114.177		87.115		119.481		66.968
	1300	-86.452	-27.218	-94.469	-48.457	-21.676	-59.634	-2.501	-21.971	-109.485	-153.261	-352.341	-130.042	32.416		-7.617		112.628		85.410		117.426		65.394
	1400	-86.413	-27.376	-94.515	-48.470	-21.682	-59.734	-2.491	-22.050	-109.341	-153.085	-350.372	-129.892	32.358		-7.405		110.874		83.498		115.159		63.617
	1500	-86.373	-27.537	-94.562	-48.484	-21.677	-59.824	-2.483	-22.104	-109.197	-152.901	-348.185	-129.739	32.287		-7.201		108.911		81.374		112.673		61.630
ΔF (kcal• mol^{-1})	298	-71.741	-32.783	-94.265	-39.589	-7.975	-54.636	15.955	-12.145	-88.689	-144.247	-315.910	-111.888	21.853	-16.03	-6.846	5.020	99.922	-73.276	67.139	-49.235	73.314	-53.763	52.790
	400	-71.947	-34.975	-94.335	-41.774	-8.938	-53.519	11.934	-10.066	-86.597	-141.680	-306.676	-111.446	18.544	-10.13	-5.841	3.191	93.049	-50.835	58.074	-31.727	60.071	-32.819	45.881
	500	-71.923	-37.144	-94.339	-43.726	-9.616	-52.361	8.369	-7.845	-84.310	-139.184	-297.458	-110.844	15.217	-6.65	-4.834	2.113	86.351	-37.741	49.207	-21.507	46.842	-20.473	39.182
	600	-71.790	-39.311	-94.458	-45.587	-10.149	-51.156	4.987	-5.493	-81.919	-136.720	-288.202	-110.168	11.845	-4.31	-3.991	1.454	79.692	-29.025	40.381	-14.708	33.549	-12.219	32.463
	700	-71.562	-41.468	-94.510	-47.358	-10.558	-49.915	1.779	-3.046	-79.441	-134.284	-278.965	-109.452	8.447	-2.64	-3.127	0.976	73.119	-22.827	31.651	-9.881	20.277	-6.330	25.864
	800	-72.574	-43.612	-94.556	-50.368	-12.183	-48.646	-3.910	-0.533	-78.213	-131.845	-270.945	-109.877	5.034	-1.38	-2.298	0.628	66.526	-18.173	22.914	-6.259	8.264	-2.257	19.248
	900	-70.822	-45.744	-94.596	-50.615	-11.027	-47.352	-4.078	2.029	-74.230	-129.402	-260.311	-107.602	1.608	-0.39	-1.500	0.364	60.087	-14.590	14.343	-3.483	-6.323	1.535	12.789
	1000	-69.071	-47.859	-94.628	-50.859	-9.861	-46.040	-4.247	4.625	-70.260	-126.957	-249.773	-105.323	-1.819	0.40	-0.729	0.159	53.745	-11.745	5.886	-1.286	-20.761	4.537	6.431
	1100	-67.326	-49.962	-94.658	-51.104	-8.689	-44.712	-4.421	7.247	-66.306	-124.507	-239.336	-103.036	-5.250	1.04	0.016	-0.003	47.503	-9.437	-2.459	0.489	-35.057	6.965	0.174
	1200	-65.582	-52.049	-94.681	-51.345	-7.511	-43.371	-4.591	9.887	-62.360	-121.894	-228.853	-100.585	-8.678	1.58	0.739	-0.135	41.377	-7.535	-10.672	1.943	-49.188	8.958	-5.963
	1300	-63.840	-54.126	-94.701	-51.586	-6.330	-42.022	-4.763	12.535	-58.426	-119.273	-218.487	-96.125	-12.104	2.03	1.447	-0.243	35.374	-5.946	-18.752	3.152	-63.164	10.618	-11.977
	1400	-62.102	-56.189	-94.716	-51.825	-5.149	-40.663	-4.937	15.195	-54.504	-116.665	-208.261	-95.675	-15.526	2.42	2.136	-0.333	29.494	-4.604	-26.695	4.167	-76.971	12.015	-17.864
	1500	-60.369	-58.241	-94.728	-52.066	-3.971	-39.297	-5.116	17.859	-50.593	-114.070	-198.187	-93.236	-18.944	2.76	2.810	-0.409	23.748	-3.460	-34.493	5.025	-90.606	13.200	-23.616

TABLE II (Continued)

Thermodynamic Data for SO_2 Reduction Reactions

Log K_{19}	Eq 20	Log K_{20}	Eq 21	Log K_{21}	Eq 21-2	Log K_{21-2}	Eq 22	Log K_{22}	Eq 22-2	Log K_{22-2}	Eq 23	Log K_{23}	Eq 24	Log K_{24}	Eq 25	Log K_{25}	Eq 26	Log K_{26}	Eq 27	Log K_{27}	Eq 28	Log K_{28}	Eq 29	Log K_{29}
	52.440		62.225		17.576		178.099		66.798		52.113		123.776		41.552		-40.672		-1.532		37.905		74.900	
	52.178		61.888		17.568		177.982		67.928		52.351		124.454		41.586		-41.282		-2.442		38.208		77.598	
	51.969		61.484		17.286		177.470		68.581		52.430		124.431		41.441		-41.549		-3.485		38.294		79.599	
	51.682		60.974		16.798		176.506		68.882		52.308		124.028		41.108		-41.812		-4.644		38.148		81.124	
	51.286		60.336		16.122		175.028		68.852		51.970		123.285		40.583		-42.119		-5.919		37.761		82.245	
	50.686		59.485		28.268		172.798		81.516		51.349		122.251		39.871		-42.509		-7.313		37.136		135.011	
	49.990		58.539		26.948		170.187		80.602		50.573		120.956		38.964		-43.028		-8.832		36.273		134.288	
	49.120		57.424		25.485		166.983		79.442		49.574		119.423		37.865		-43.693		-10.477		35.176		133.371	
	48.066		56.132		23.874		163.178		78.047		48.360		117.655		36.569		-44.517		-12.253		33.854		132.255	
	46.820		54.658		22.110		158.766		76.421		46.926		115.662		35.072		-45.518		-14.166		32.307		130.938	
	45.377		52.994		20.178		153.735		74.565		45.272		113.427		33.361		-46.705		-16.237		30.533		129.423	
	43.735		51.140		18.085		148.094		72.493		43.406		110.976		31.450		-48.076		-18.456		28.547		127.708	
	41.886		49.087		15.812		141.828		70.203		41.325		108.298		29.322		-49.654		-20.850		26.340		125.798	
-38.712	38.440	-28.189	45.286	-33.209	7.755	-5.687	115.220	-84.494	41.753	-30.619	26.932	-19.750	72.890	-53.452	15.492	-11.361	-41.906	30.731	-14.522	10.649	12.630	-9.262	74.586	-54.696
-25.066	33.689	-18.405	39.530	-21.596	4.439	-2.425	93.681	-51.181	33.049	-18.056	18.270	-9.981	55.330	-30.228	6.560	-3.584	-42.210	23.061	-18.846	10.296	3.923	-2.143	74.294	-40.589
-17.125	29.156	-12.743	33.990	-14.856	1.191	-0.521	72.671	-31.762	24.253	-10.600	9.803	-4.285	38.038	-16.625	-2.064	0.902	-42.166	18.429	-22.830	9.978	-4.602	2.011	73.254	-32.017
-11.824	24.545	-8.940	28.536	-10.393	-1.986	0.723	51.790	-18.863	15.352	-5.591	1.212	-0.441	20.790	-7.572	-10.882	3.963	-42.554	15.499	-26.590	9.685	-13.243	4.823	71.826	-26.160
-8.074	20.077	-6.268	23.204	-7.244	-5.064	1.581	31.190	-9.737	6.429	-2.007	-7.256	2.265	3.641	-1.137	-19.507	6.090	-42.655	13.316	-30.147	9.412	-21.791	6.600	70.185	-21.911
-5.258	15.582	-4.256	17.880	-4.884	-6.838	1.868	10.561	-2.885	-1.271	0.347	-15.752	4.303	-13.380	3.655	-28.044	7.661	-42.708	11.666	-33.516	9.155	-30.247	8.262	73.196	-19.995
-3.105	11.235	-2.728	12.735	-3.092	-11.147	2.707	-9.568	2.323	-11.568	2.809	-24.095	5.851	-30.267	7.349	-36.483	8.859	-42.699	10.368	-36.699	8.911	-38.620	9.377	65.509	-15.906
-1.405	6.976	-1.524	7.705	-1.684	-15.304	3.344	-29.369	6.419	-21.748	4.753	-32.338	7.067	-46.986	10.268	-44.906	9.792	-42.626	9.315	-39.710	8.678	-46.883	10.245	57.914	-12.656
-0.035	2.807	-0.558	2.791	-0.554	-19.307	3.836	-48.836	9.702	-31.804	6.318	-40.477	8.041	-63.548	12.625	-53.016	10.532	-42.484	8.440	-42.548	8.453	-55.029	10.932	50.416	-10.016
1.086	-1.255	0.229	-1.994	0.363	-23.154	4.217	-67.918	12.369	-41.719	7.597	-48.491	8.831	-79.928	14.556	-61.094	11.126	-42.260	7.696	-45.216	8.234	-63.042	11.481	43.032	-7.837
2.013	-5.201	0.874	-6.648	1.118	-26.852	4.514	-86.605	14.558	-51.491	8.656	-56.374	9.477	-94.142	15.825	-67.040	11.269	-39.938	6.714	-45.726	7.687	-68.918	11.585	29.770	-5.004
2.788	-9.033	1.410	-11.169	1.743	-30.393	4.744	-104.891	16.373	-61.114	9.540	-64.127	10.010	-112.170	17.509	-76.846	11.995	-41.522	6.481	-50.066	7.815	-79.651	12.277	28.626	-4.468
3.441	-12.739	1.856	-15.549	2.265	-33.774	4.920	-122.747	17.883	-70.577	10.282	-71.738	10.451	-128.013	18.650	-84.505	12.311	-40.997	5.973	-52.237	7.610	-86.230	12.563	21.615	-3.149

TABLE II (Continued)

Thermodynamic Data for SO_2 Reduction Reactions

Eq 30	Log K_{30}	Eq 31	Log K_{31}	Eq 32	Log K_{32}	Eq 33	Log K_{33}	Eq 34	Log K_{34}	Eq 35	Log K_{35}	Eq 36	Log K_{36}	Log K_{39}	Log K_{40}	Log K_{41}	Log K_{42}	Log K_{43}	Eq 44	Log K_{44}	Eq 45	Log K_{45}	Eq 46	Log K_{46}
250.432		-6.433		14.208		-109.637		23.993		87.766		338.198							-34.849		-23.107		18.005	
249.994		-4.300		14.143		-109.796		23.853		86.198		336.192							-32.586		-22.306		19.128	
249.421		-2.656		14.136		-109.862		23.652		84.911		334.332							-30.928		-21.735		19.760	
248.540		-1.292		14.160		-109.882		23.452		83.708		332.248							-29.612		-21.300		20.160	
247.263		-0.132		14.209		-109.875		23.259		82.509		329.772							-28.550		-20.963		20.388	
245.253		39.945		14.213		-109.917		23.012		55.121		300.374							11.519		-7.625		33.565	
242.988		39.969		14.300		-109.881		22.849		54.350		297.338							11.369		-7.693		33.303	
240.173		39.985		14.398		-109.837		22.702		53.401		293.574							11.189		-7.768		33.011	
236.781		39.996		14.506		-109.788		22.572		52.263		289.044							10.984		-7.847		32.696	
232.798		40.004		14.619		-109.733		22.457		50.930		283.728							10.766		-7.929		32.366	
228.213		40.014		14.739		-109.671		22.356		49.395		277.608							10.536		-8.017		32.016	
223.016		40.027		14.859		-109.606		22.264		47.654		270.670							10.309		-8.102		31.661	
217.198		40.049		14.985		-109.535		22.186		45.700		262.898							10.079		-8.189		31.299	
195.666	-143.487	7.023	-5.150	14.302	-10.488	-104.100	76.339	21.148	-15.508	60.540	-44.396	256.206	-187.883	52.610	65.038	5.848	29.032	-11.700	-21.581	15.826	-22.524	16.517	6.175	-4.528
176.966	-96.682	11.479	-6.271	14.347	-7.838	-102.181	55.824	20.188	-11.029	51.336	-28.046	228.302	-124.728	39.307	47.310	4.883	22.822	-6.520	-17.215	9.405	-22.388	12.231	1.997	-1.091
158.790	-69.401	15.243	-6.662	14.405	-6.296	-100.263	43.821	19.239	-8.409	42.768	-18.692	201.558	-88.094	31.435	36.849	4.203	19.111	-3.658	-13.567	5.930	-22.416	9.797	-2.365	1.034
140.734	-51.258	18.686	-6.806	14.455	-5.265	-98.342	35.818	18.446	-6.718	34.454	-12.549	175.188	-63.807	26.147	29.836	3.696	16.604	-1.816	-10.224	3.724	-22.668	8.256	-6.832	2.488
122.963	-38.388	21.898	-6.836	14.525	-4.535	-96.394	30.093	17.652	-5.511	26.389	-8.238	149.352	-46.626	22.341	24.801	3.296	14.785	-0.555	-7.152	2.233	-22.948	7.164	-11.374	3.551
105.036	-28.692	28.638	-7.823	14.495	-3.960	-94.542	25.826	16.793	-4.587	15.920	-4.349	120.956	-33.041	19.825	21.365	3.328	13.759	1.068	-0.352	0.096	-21.982	6.005	-14.650	4.002
87.639	-21.280	27.222	-6.610	14.525	-3.527	-92.622	22.490	16.025	-3.891	11.065	-2.687	98.704	-23.967	17.196	18.024	2.677	12.290	0.990	-1.828	0.444	-23.774	5.773	-20.666	5.018
70.530	-15.413	25.803	-5.639	14.545	-3.179	-90.705	19.822	15.274	-3.338	6.308	-1.378	76.838	-16.792	15.094	15.354	2.155	11.114	0.928	-3.287	0.718	-25.557	5.585	-26.647	5.823
53.712	-10.671	24.384	-4.844	14.552	-2.891	-88.797	17.641	14.536	-2.888	1.648	-0.327	55.360	-10.998	13.375	13.173	1.726	10.153	0.878	-4.720	0.938	-27.332	5.430	-32.598	6.476
37.240	-6.782	22.964	-4.182	14.551	-2.650	-86.891	15.824	13.812	-2.515	-2.896	0.527	34.344	-6.254	11.943	11.356	1.368	9.350	0.836	-6.139	1.118	-29.099	5.299	-38.516	7.014
19.134	-3.216	17.544	-2.949	12.544	-2.109	-86.988	14.623	11.097	-1.865	-5.318	0.894	13.816	-2.322	10.732	9.821	1.064	8.672	0.801	-7.544	1.268	-30.861	5.188	-44.412	7.466
5.390	-0.841	20.122	-3.141	14.524	-2.267	-83.092	12.970	12.388	-1.934	-11.618	1.813	-6.228	0.972	9.694	8.508	0.804	8.090	0.771	-8.926	1.393	-32.614	5.091	-50.276	7.848
-9.959	1.451	18.701	-2.725	14.492	-2.111	-81.203	11.830	11.682	-1.702	-15.787	2.300	-25.746	3.751	8.795	7.371	0.579	7.585	0.745	-10.283	1.498	-34.359	5.006	-56.113	8.175

TABLE II (Continued)

Thermodynamic Data for SO_2 Reduction Reactions

Eq 47	Log K_{47}	Eq 48	Log K_{48}	Eq 49	Log K_{49}	Eq 50	Log K_{50}	Eq 51	Log K_{51}	Eq 52	Log K_{52}	Eq 53	Log K_{53}	Eq 54	Log K_{54}	Eq 55	Log K_{55}	Eq 56	Log K_{56}	Eq 57	Log K_{57}	Eq 58	Log K_{58}	Eq 59
-64.219		-44.649		-54.434		-35.503		-51.001		-17.236		44.432		-78.904		-49.549		-69.119		-0.327		-19.931		-51.258
-63.740		-44.320		-54.030		-32.240		-48.906		-17.166		44.985		-79.317		-50.187		-69.607		0.173		-20.013		-51.737
-63.230		-44.198		-53.714		-30.004		-47.380		-17.139		45.104		-79.381		-50.833		-69.865		0.462		-20.144		-52.123
-62.760		-44.176		-53.468		-28.360		-46.148		-17.144		45.046		-79.334		-51.458		-70.042		0.626		-20.314		-52.482
-62.314		-44.214		-53.264		-27.182		-45.126		-17.169		44.857		-79.196		-52.046		-70.146		0.684		-20.507		-52.908
-48.815		-31.217		-40.016		12.845		-5.049		-17.197		44.588		-78.982		-52.585		-70.183		0.663		-20.709		-53.100
-48.689		-31.591		-40.140		12.535		-5.149		-17.224		44.270		-78.718		-53.071		-70.169		0.583		-20.914		-53.361
-48.547		-31.939		-40.243		12.097		-5.253		-17.247		43.922		-78.415		-53.503		-70.111		0.454		-21.111		-53.586
-48.390		-32.258		-40.324		11.572		-5.358		-17.262		43.552		-78.077		-53.879		-70.011		0.294		-21.297		-53.774
-48.224		-32.548		-40.386		10.978		-5.464		-17.277		43.166		-77.719		-54.205		-69.881		0.106		-21.471		-53.928
-48.050		-32.816		-40.433		10.326		-5.572		-17.293		42.756		-77.343		-54.492		-69.726		-0.105		-21.639		-54.055
-47.865		-33.055		-40.460		9.651		-5.677		-17.308		42.337		-76.952		-54.737		-69.547		-0.329		-21.791		-54.149
-47.677		-33.275		-40.476		8.957		-5.783		-17.323		41.909		-76.555		-54.952		-69.354		-0.561		-21.935		-54.222
-51.223	37.563	-37.531	27.522	-44.377	32.543	-44.597	32.704	-37.611	27.581	-22.996	16.863	20.053	-14.705	-66.044	48.432	-45.506	33.371	-59.198	43.411	-11.508	8.439	-22.484	16.488	-44.337
-46.773	25.553	-35.091	19.171	-40.932	22.362	-48.053	26.253	-33.175	18.124	-24.974	13.644	11.603	-6.339	-61.552	33.628	-44.029	24.054	-55.711	30.437	-15.419	8.424	-23.346	12.755	-41.890
-42.467	18.561	-32.799	14.335	-37.633	16.448	-52.273	22.847	-29.303	12.807	-26.841	11.731	3.236	-1.414	-56.917	24.876	-42.415	18.538	-52.083	22.764	-19.353	8.458	-24.164	10.561	-39.381
-38.504	14.024	-30.522	11.117	-34.513	12.570	-56.890	20.720	-25.952	9.452	-28.890	10.522	-5.136	1.871	-52.644	19.174	-40.671	14.813	-48.653	17.720	-23.333	8.498	-24.953	9.088	-36.798
-34.522	10.777	-28.268	8.825	-31.395	9.801	-61.818	19.299	-22.742	7.100	-30.846	9.630	-13.485	4.210	-48.207	15.050	-38.826	12.121	-45.080	14.073	-27.333	8.533	-25.711	8.027	-34.158
-29.314	8.008	-24.718	6.752	-27.016	7.380	-63.020	17.215	-15.802	4.317	-32.797	8.959	-21.799	5.955	-43.795	11.963	-36.901	10.080	-41.497	11.336	-31.334	8.559	-26.440	7.222	-31.474
-26.882	6.527	-23.882	5.799	-25.382	6.163	-72.488	17.601	-17.140	4.162	-34.747	8.437	-30.085	7.305	-39.409	9.569	-34.909	8.476	-37.909	9.205	-35.330	8.579	-27.145	6.591	-28.753
-24.467	5.347	-23.009	5.028	-23.738	5.188	-81.915	17.901	-18.467	4.036	-36.692	8.018	-38.327	8.376	-35.057	7.661	-32.870	7.183	-34.328	7.502	-39.314	8.591	-27.828	6.081	-26.009
-22.066	4.384	-22.098	4.390	-22.082	4.387	-91.288	18.136	-19.782	3.930	-38.638	7.676	-46.537	9.245	-30.739	6.107	-30.787	6.116	-30.755	6.110	-43.284	8.599	-28.490	5.660	-23.240
-19.682	3.584	-21.160	3.853	-20.421	3.719	-100.610	18.322	-21.090	3.841	-40.580	7.390	-54.705	9.962	-26.454	4.819	-28.671	5.221	-27.193	4.952	-47.236	8.602	-29.134	5.306	-20.456
-17.310	2.910	-20.204	3.396	-18.757	3.153	-109.890	18.473	-22.390	3.764	-42.519	7.148	-62.846	10.564	-22.193	3.731	-26.534	4.460	-23.640	3.974	-51.173	8.602	-29.768	5.004	-17.664
-14.952	2.334	-19.224	3.001	-17.088	2.667	-119.114	18.593	-23.680	3.696	-44.458	6.940	-70.951	11.075	-17.965	2.804	-24.373	3.804	-20.101	3.138	-55.094	8.600	-30.386	4.743	-14.860
-12.605	1.836	-18.225	2.655	-15.415	2.246	-128.281	18.689	-24.955	3.636	-46.397	6.759	-79.028	11.513	-13.766	2.006	-22.196	3.234	-16.576	2.415	-58.999	8.595	-30.994	4.515	-12.050

TABLE II (Continued)

Thermodynamic Data for SO_2 Reduction Reactions

Log K_{59}	Eq 60	Log K_{60}	Eq 61	Log K_{61}	Eq 62	Log K_{62}	Eq 63	Log K_{63}	Eq 64	Log K_{64}	Eq 65	Log K_{65}	Eq 66	Log K_{66}	Eq 67	Log K_{67}	Eq 68	Log K_{68}	Eq 69	Log K_{69}	Eq 70	Log K_{70}	Eq 71	Log K_{71}
	-59.834		11.396		-18.264		63.960		-141.600		-92.675		-43.453		5.769		14.685		11.509		8.076		16.208	
	-59.419		11.711		-17.966		64.902		-142.268		-93.718		-43.358		7.002		15.577		13.284		8.160		16.366	
	-59.105		11.835		-17.797		65.193		-142.282		-94.702		-43.407		7.888		16.151		14.560		8.226		16.480	
	-58.898		11.854		-17.738		65.182		-142.118		-95.658		-43.574		8.510		16.574		15.588		8.268		16.550	
	-58.788		11.794		-17.763		64.939		-141.816		-96.566		-43.836		8.894		16.882		16.426		8.288		16.576	
	-58.757		11.682		-17.836		64.544		-141.406		-97.411		-44.163		9.085		30.167		43.251		8.284		16.558	
	-58.791		11.533		-17.949		64.043		-140.937		-98.192		-44.538		9.116		30.029		43.250		8.259		16.499	
	-58.875		11.364		-18.079		63.479		-140.416		-98.896		-44.939		9.018		29.868		43.211		8.221		16.414	
	-58.992		11.180		-18.221		62.865		-139.850		-99.520		-45.347		8.826		29.687		43.137		8.171		16.304	
	-59.136		10.986		-18.370		62.220		-139.255		-100.065		-45.754		8.557		29.495		43.037		8.115		16.183	
	-59.302		10.777		-18.535		61.531		-138.634		-100.549		-46.162		8.225		29.293		42.915		8.054		16.052	
	-59.475		10.567		-18.695		60.831		-137.984		-100.959		-46.551		7.857		29.087		42.776		7.993		15.920	
	-59.655		10.352		-18.861		60.115		-137.325		-101.320		-46.929		7.462		28.878		42.624		7.931		15.785	
32.514	-64.975	47.648	-0.631	0.463	-29.093	21.335	28.305	-20.757	-115.190	84.472	-80.960	59.370	-46.962	34.439	-12.964	9.507	14.821	-10.869	14.781	-10.839	8.015	-5.878	16.898	-12.392
22.886	-66.799	36.494	-4.802	2.623	-32.842	17.943	15.928	-8.702	-105.997	57.909	-76.792	41.954	-48.182	26.323	-19.572	10.693	14.779	-8.074	15.737	-8.598	7.980	-4.360	17.107	-9.346
17.212	-68.680	30.017	-8.947	3.910	-36.463	15.937	3.639	-1.590	-96.616	42.227	-72.446	31.663	-49.384	21.584	-26.322	11.504	14.450	-6.316	16.198	-7.080	7.868	-3.439	17.218	-7.525
13.403	-70.616	25.720	-13.108	4.774	-40.349	14.696	-8.677	3.160	-87.857	31.999	-67.902	24.731	-50.564	18.416	-33.226	12.102	14.140	-5.150	16.425	-5.982	7.864	-2.864	17.431	-6.349
10.664	-72.580	22.659	-17.264	5.390	-44.117	13.773	-20.969	6.546	-78.839	24.613	-63.204	19.732	-51.711	16.144	-40.218	12.556	13.685	-4.272	16.448	-5.135	7.795	-2.434	17.575	-5.487
9.598	-74.553	20.365	-21.406	5.847	-47.874	13.077	-33.210	9.072	-69.870	19.086	-58.380	15.947	-52.813	14.427	-47.246	12.906	14.481	-3.956	18.939	-5.173	7.725	-2.110	17.720	-4.840
6.982	-76.526	18.581	-25.537	6.201	-51.626	12.535	-45.410	11.026	-60.950	14.799	-53.450	12.978	-53.871	13.081	-54.292	13.183	12.527	-3.042	15.898	-3.860	7.656	-1.859	17.868	-4.339
5.684	-78.493	17.153	-29.647	6.479	-55.361	12.098	-57.541	12.575	-52.091	11.384	-48.446	10.587	-54.890	11.995	-61.334	13.403	10.590	-2.314	12.861	-2.811	7.590	-1.659	18.023	-3.939
4.617	-80.449	15.982	-33.740	6.703	-59.085	11.738	-69.617	13.830	-43.287	8.600	-43.367	8.616	-55.864	11.098	-68.361	13.581	8.673	-1.723	9.831	-1.953	7.531	-1.496	18.191	-3.614
3.725	-82.392	15.004	-37.812	6.886	-62.789	11.434	-81.623	14.864	-34.538	6.290	-38.233	6.963	-56.798	10.343	-75.363	13.724	6.772	-1.233	6.807	-1.240	7.476	-1.361	18.370	-3.345
2.969	-84.325	14.175	-41.872	7.039	-66.485	11.176	-93.587	15.732	-25.832	4.342	-33.067	5.559	-57.706	9.700	-82.345	13.842	4.883	-0.821	3.790	-0.637	7.423	-1.248	18.554	-3.119
2.320	-86.244	13.462	-45.912	7.167	-70.165	10.952	-105.489	16.466	-17.179	2.682	-27.859	4.349	-58.580	9.144	-89.301	13.939	3.013	-0.470	0.785	-0.123	7.377	-1.152	18.751	-2.927
1.756	-88.150	12.842	-49.938	7.275	-73.834	10.757	-117.342	17.095	-8.572	1.249	-22.622	3.296	-59.425	8.657	-96.228	14.019	1.161	-0.169	-2.204	0.321	7.336	-1.069	18.960	-2.762

TABLE II (Concluded)

Thermodynamic Data for SO_2 Reduction Reactions

Eq 72	Log K_{72}	Eq 73	Log K_{73}	Eq 74	Log K_{74}	Eq 75	Log K_{75}	Eq 76	Log K_{76}	Eq 77	Log K_{77}	Eq 78	Log K_{78}	Eq 79	Log K_{79}	Eq 80	Log K_{80}	Eq 81	Log K_{81}	Eq 82	Log K_{82}	Eq 83	Log K_{83}
-77.846		-51.375		-175.547		-6.609		3.176		-130.781		-3.377		-69.751		41.168		9.841		-56.533		-196.315	
-77.704		-51.386		-175.152		-7.417		2.293		-131.183		-5.078		-70.802		41.480		9.756		-55.968		-196.492	
-77.611		-51.313		-174.849		-7.925		1.591		-131.461		-6.306		-71.565		41.523		9.544		-55.715		-196.683	
-77.574		-51.242		-174.658		-8.306		0.986		-131.722		-7.306		-72.222		41.474		9.306		-55.610		-196.842	
-77.593		-51.184		-174.584		-8.594		0.456		-131.994		-8.138		-72.828		41.351		9.050		-55.640		-196.984	
-77.660		-51.146		-174.613		-21.883		-13.084		-145.350		-34.977		-99.539		41.180		8.789		-55.773		-197.114	
-77.771		-51.134		-174.732		-21.770		-13.221		-145.368		-35.010		-99.524		40.977		8.530		-55.984		-197.228	
-77.907		-51.136		-174.917		-21.647		-13.343		-145.428		-35.018		-99.553		40.751		8.276		-56.259		-197.334	
-78.067		-51.153		-175.153		-21.516		-13.450		-145.516		-35.004		-99.613		40.505		8.028		-56.581		-197.435	
-78.236		-51.174		-175.420		-21.380		-13.542		-145.626		-34.969		-99.696		40.248		7.791		-56.936		-197.530	
-78.417		-51.199		-175.714		-21.239		-13.622		-145.754		-34.917		-99.798		39.977		7.561		-57.320		-197.621	
-78.595		-51.219		-176.013		-21.094		-13.689		-145.888		-34.849		-99.909		39.697		7.339		-57.721		-197.711	
-78.777		-51.240		-176.321		-20.947		-13.746		-146.028		-34.770		-100.027		39.411		7.124		-58.133		-197.800	
-77.367	56.735	-44.584	32.695	-174.494	127.961	-6.806	4.991	0.040	-0.029	-136.716	100.258	-5.898	4.325	-81.172	59.526	29.567	-21.682	7.714	-5.657	-67.560	49.544	-192.220	140.960
-77.228	42.192	-42.253	23.084	-174.200	95.170	-6.799	3.714	-0.958	0.523	-138.746	75.801	-6.610	3.611	-85.038	46.459	25.532	-13.949	6.988	-3.818	-71.440	39.030	-190.803	104.241
-77.121	33.707	-39.977	17.472	-173.998	76.048	-6.582	2.877	-1.748	0.764	-140.603	61.452	-6.848	2.993	-88.508	38.684	21.533	-9.411	6.316	-2.760	-75.344	32.930	-189.359	82.762
-77.027	28.055	-37.716	13.737	-173.846	63.318	-6.276	2.286	-2.285	0.832	-142.406	51.867	-6.858	2.498	-91.832	33.447	17.539	-6.388	5.694	-2.074	-79.280	28.875	-187.878	68.429
-76.935	24.018	-35.467	11.072	-173.719	54.233	-5.890	1.839	-2.763	0.863	-144.142	44.999	-6.668	2.082	-95.005	29.659	13.559	-4.233	5.112	-1.596	-83.225	25.982	-186.371	58.183
-76.836	20.989	-33.224	9.076	-173.595	47.420	-6.756	1.845	-4.458	1.218	-147.127	40.190	-8.944	2.443	-100.669	27.499	9.602	-2.623	4.568	-1.248	-87.157	23.808	-184.850	50.494
-76.728	18.631	-30.984	7.523	-173.461	42.119	-4.871	1.183	-3.371	0.819	-147.348	35.778	-5.686	1.381	-100.811	24.478	5.664	-1.375	4.056	-0.985	-91.069	22.113	-183.310	44.510
-76.605	16.741	-28.746	6.282	-173.310	37.874	-3.000	0.656	-2.271	0.496	-147.564	32.247	-2.428	0.531	-100.952	22.061	1.753	-0.383	3.572	-0.781	-94.952	20.750	-181.754	39.719
-76.467	15.191	-26.505	5.266	-173.138	34.396	-1.142	0.227	-1.158	0.230	-147.775	29.358	0.829	-0.165	-101.092	20.083	-2.137	0.425	3.113	-0.618	-98.808	19.630	-180.193	35.798
-76.311	13.897	-24.262	4.418	-172.940	31.494	0.704	-0.128	-0.035	0.006	-147.974	26.947	4.087	-0.744	-101.220	18.433	-5.999	1.092	2.679	-0.488	-102.628	18.690	-178.622	32.529
-76.147	12.800	-22.021	3.702	-172.726	29.035	2.540	-0.427	1.093	-0.184	-148.165	24.907	7.341	-1.234	-101.342	17.036	-9.843	1.655	2.261	-0.380	-106.422	17.890	-177.043	29.761
-75.965	11.858	-19.776	3.087	-172.486	26.924	4.364	-0.681	2.228	-0.348	-148.346	23.156	10.589	-1.653	-101.458	15.837	-13.665	2.133	1.861	-0.290	-110.186	17.199	-175.456	27.388
-75.768	11.038	-17.527	2.553	-172.221	25.090	6.175	-0.900	3.365	-0.490	-148.519	21.637	13.828	-2.015	-101.569	14.797	-17.466	2.545	1.478	-0.215	-113.919	16.597	-173.863	25.330

Further oxidation to CO_2 from CO (equation 16) is a favorable reaction at lower temperatures; however, the reaction kinetic is expected to be slower at a lower temperature, as compared to a higher temperature reaction. The log Kp value is decreased slowly when the temperature is increased, and it remains at about zero thereafter (Figure 1). This indicates that Kp = 1 or $P_{CO2} \cdot P_{H2} = P_{CO} \cdot P_{H2O}$ at the equilibrium state.

The decomposition reactions of $CaSO_4$ to produce CaO as the final product may be expressed by the following possible reaction routes:

$$CaSO_4 \rightarrow CaO + SO_2 + 0.5O_2 \qquad (17)$$

$$CaSO_4 + C \rightarrow CaO + SO_2 + CO \qquad (18)$$

$$CaSO_4 + 0.5C \rightarrow CaO + SO_2 + 0.5CO_2 \qquad (19)$$

$$CaSO_4 + CO \rightarrow CaO + SO_2 + CO_2 \qquad (20)$$

$$CaSO_4 + H_2 \rightarrow CaO + SO_2 + H_2O \qquad (21)$$

$$3CaSO_4 + CH_4 \rightarrow 3CaO + 3SO_2 + 2H_2O + CO \qquad (22)$$

$$CaSO_4 + CH_4 \rightarrow CaO + H_2S + H_2O + CO_2 \qquad (23)$$

Direct decomposition of $CaSO_4$ is a very unfavorable reaction (equation 17), as indicated by the small K_p, value (Figure 1) at all temperatures.

However, the addition of carbon (equations 18-19) to the system increased the K_p value and resulted in a more favorable reaction above 1200°K, regardless of the final carbon product (either CO or CO_2, Figure 2). Other reducing agents, such as CO (equation 20), H_2 (equation 21), and CH_4 (equations 22-23) were equally effective in decomposing $CaSO_4$; CH_4 required the lowest temperature (Figure 2).

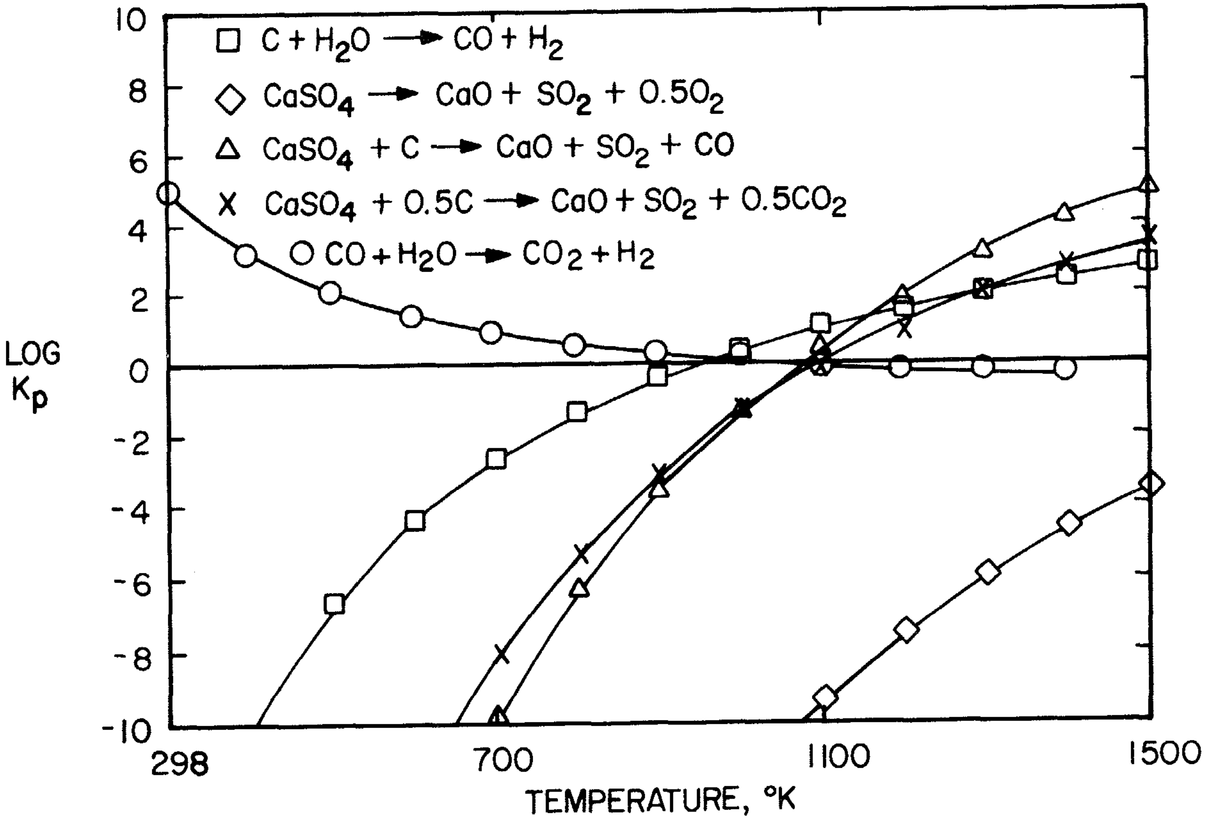

Figure 1. Relationship between reaction temperature and equilibrium constant for equations 15-19.

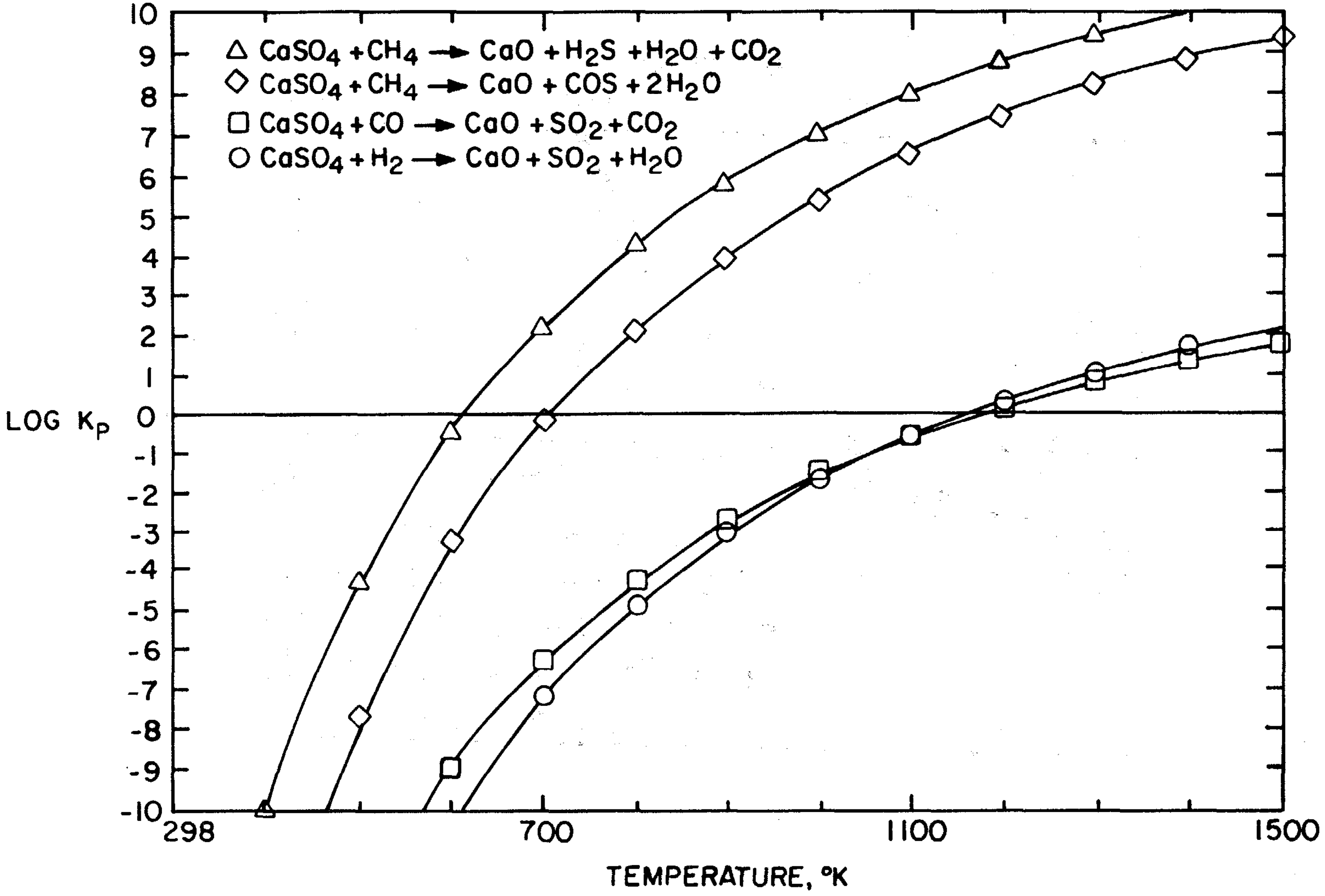

Figure 2. Relationship between reaction temperature and equilibrium constant for equations 20-23.

The decomposition reaction of $CaSO_4$ to produce CaO and elemental sulfur as the final products is depicted as the following reactions:

$$CaSO_4 + 3C \rightarrow CaO + 0.5S_2 + 3CO \tag{18-2}$$

$$CaSO_4 + 3H_2 \rightarrow CaO + 0.5S_2 + 3H_2O \tag{21-2}$$

$$CaSO_4 + CH4 \rightarrow CaO + 0.5S_2 + 2H_2O + CO \tag{22-2}$$

It is noted that the stoichiometric requirement for the reducing agent (carbon, hydrogen, or methane) to produce elemental sulfur is three times as much as the reactions which produce SO_2 as the final product (equations 18 versus 18-2, 21 versus 21-2, and 22 versus 22-2). All three reactions are favorable above 800°K, which indicates that there is a possibility to go to elemental sulfur directly from $CaSO_4$ if reaction conditions are right (Figure 3).

Anhydrite also may be reduced to CaS as the final product by the following reactions:

$$CaSO_4 + 4C \rightarrow CaS + 4CO \tag{24}$$

$$CaSO_4 + 2C \rightarrow CaS + 2CO_2 \tag{25}$$

$$CaSO_4 + 4CO \rightarrow CaS + 4CO_2 \tag{26}$$

$$CaSO_4 \quad 4H_2 \rightarrow CaS + 4H_2O \tag{27}$$

$$CaSO_4 \quad CH4 \rightarrow CaS + CO_2 + 2H_2O \tag{28}$$

All four reactions were favorable, as shown in Figure 4. They required lower temperatures than those reactions which produce CaO and SO_2 (Figure 2 versus Figure 4). From this analysis, an important conclusion may be drawn on the basis of the equilibrium data. Anhydrite can be more readily decomposed by

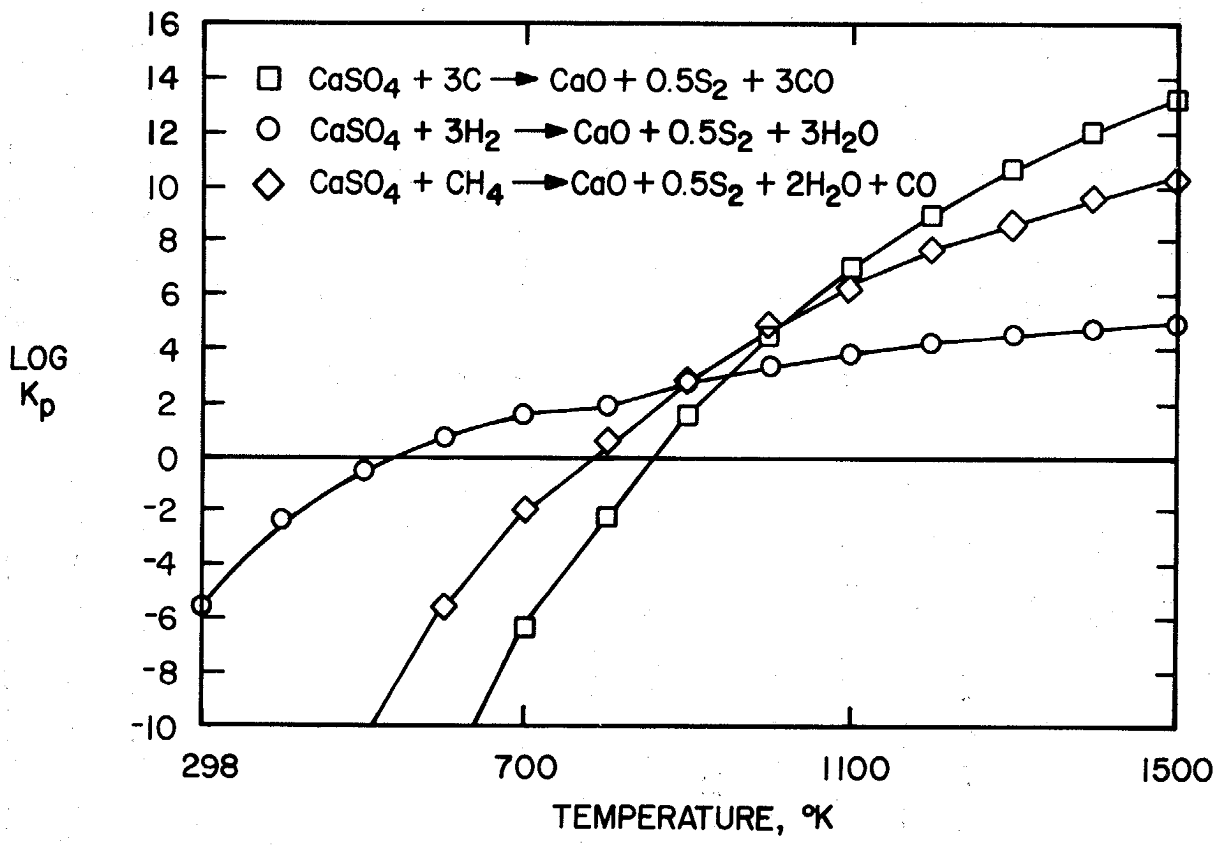

Figure 3. Relationship between reaction temperature and equilibrium constant for equations 18-2, 21-2, and 22-2.

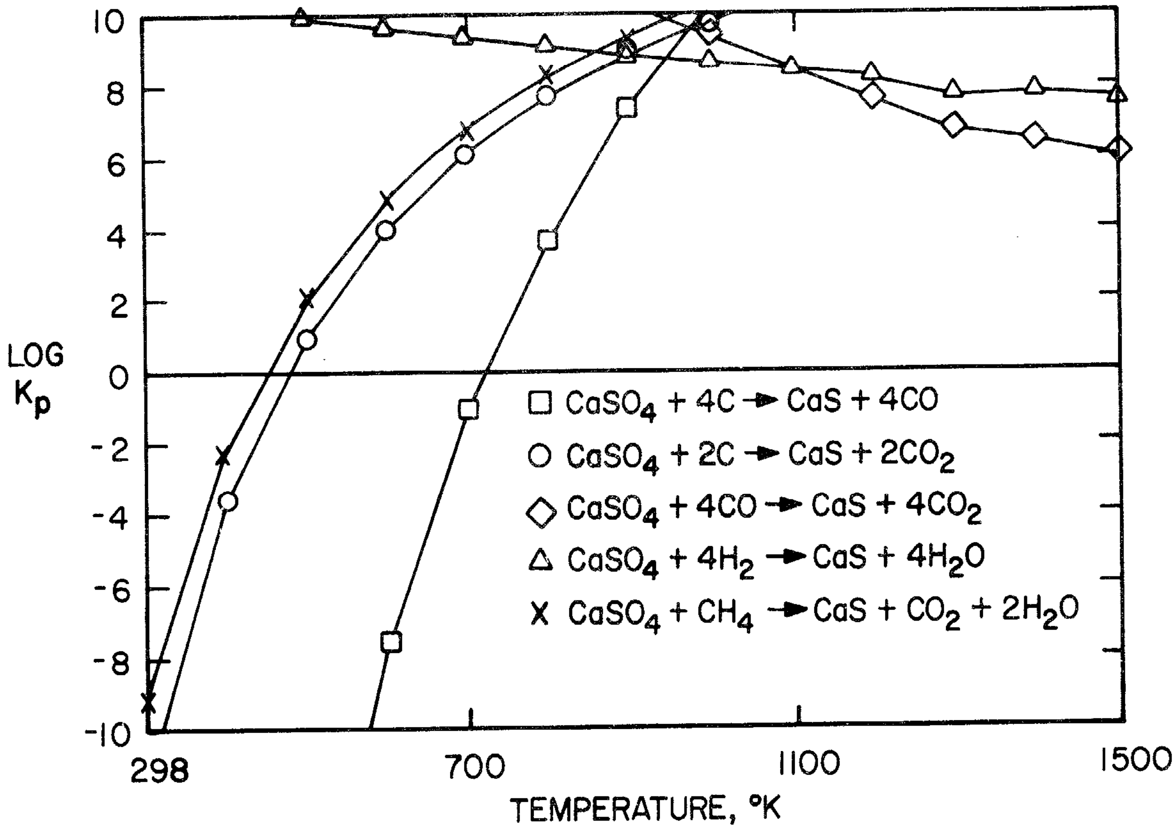

Figure 4. Relationship between reaction temperature and equilibrium constant for equations 24-28.

reducing agents, and the final products will depend on the reaction temperature. At lower temperatures (<1000°K) the predominant product will be CaS, whereas higher temperatures (>1000°K) will produce CaO and SO_2. The temperature range for which the shift of final product occurred may vary, depending on the reaction system and its kinetic parameter, but the conversion of CaS to CaO will be accelerated by increasing the reaction temperature in all systems.

Several possible reaction routes of CaS conversion to Ca0 were evaluated since CaS is the most probable intermediate product produced from $CaSO_4$ at lower temperatures. It also was sufficiently stable to be treated as a distinct raw material for other reactions:

$$3CaS + CaSO_4 \rightarrow 4CaO + 2S_2 \tag{29}$$

$$CaS + 3CaSO_4 \rightarrow 4CaO + 4SO_2 \tag{30}$$

$$2CaS + SO_2 \rightarrow 2CaO + 1.5\ S_2 \tag{31}$$

$$CaS + H_2O \rightarrow CaO \quad H_2S \tag{32}$$

$$CaS + 1.5\ O_2 \rightarrow CaO + SO_2 \tag{33}$$

$$CaS + H_2 + CO_2 \rightarrow CaO + H_2S + CO \tag{34}$$

Sulfur production from CaS with either $CaSO_4$ (equation 29) or SO_2 (equation 31) is an unfavorable reaction route, but may produce SO_2 in combination with $CaSO_4$ at high temperature (equation 30, Figure 5). Direct reaction with water (equation 32) to produce H_2S showed little promise, but the reaction will produce SO_2 with oxygen (equation 33).

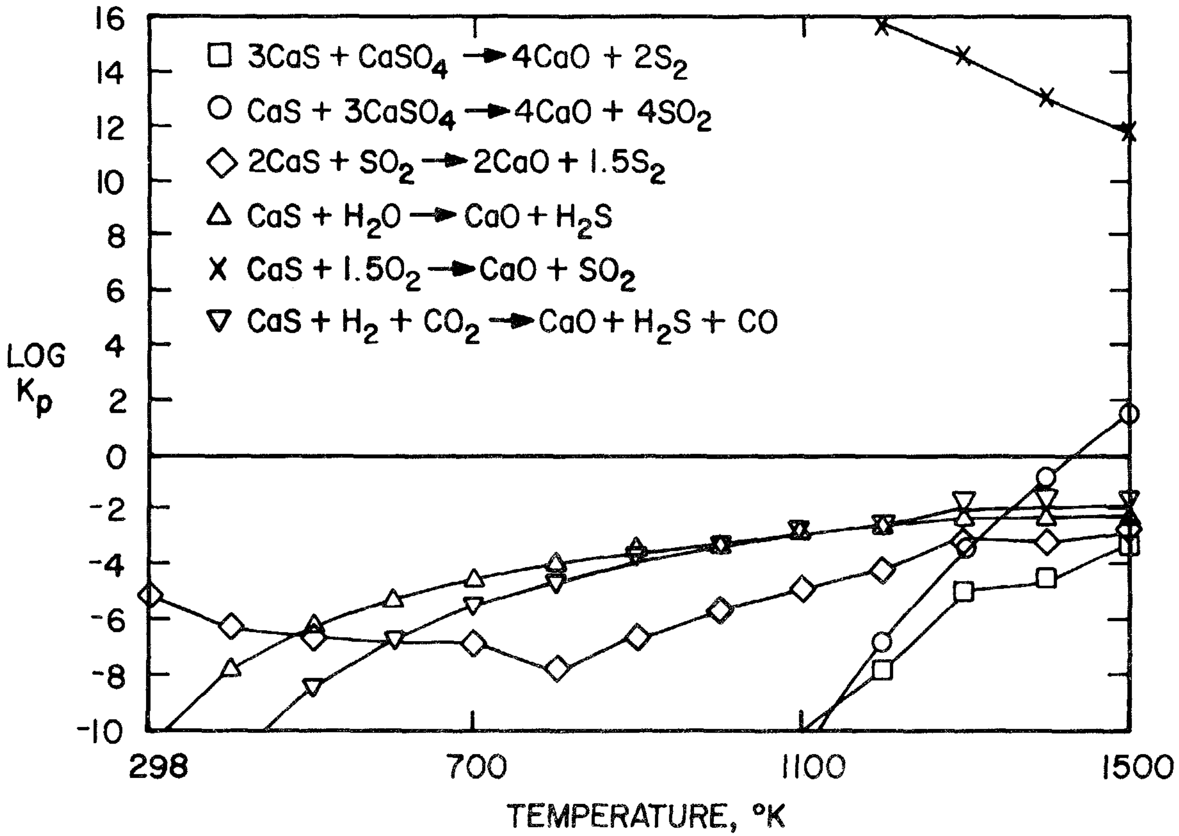

Figure 5. Relationship between reaction temperature and equilibrium constant for equations 29-34.

However, in the presence of carbon, CaS may proceed to H_2S through the reaction sequence of equations 15, 16, and 34. Even though reaction 34 itself is not favorable, the combination of the three reactions (which may occur simultaneously at the reaction site) make the overall reaction favorable. This analysis suggests that homogeneous mixtures of $CaSO_4$ with excess carbon will be converted to CaS in the first step, according to the combination of reaction mechanisms of equations 24-25. Then the CaS product will be converted to CaO and H_2S in a second-stage reaction by the introduction of steam, according to the simultaneous reaction mechanism of equations 15, 16, and 34.

Equilibrium constants for sulfur reactions with $CaSO_4$ were evaluated:

$$S_2 + CaSO_4 \rightarrow CaS + 2SO_2 \qquad (35)$$

$$S_2 + 4CaSO_4 \rightarrow 4CaO + 6SO_2 \qquad (36)$$

Both of these reactions were favorable at high temperatures only (Figure 6). The formation of CaO (equation 36) was more favorable than the formation of CaS (equation 35) at extremely high temperatures. Therefore, sulfur formed during a $CaSO_4$ reduction reaction may recombine with unreacted $CaSO_4$ to form CaO and SO_2 at high temperatures when a large excess of $CaSO_4$ is available for the reaction and a small fraction of the sulfur is converted to CaS at the same time.

Calcium oxide is a well-known absorbant for SO_2, and it forms $CaSO_3$ (equation 37). Calcium sulfite then is converted to $CaSO_4$ and CaS by a disproportionation reaction (equation 38):

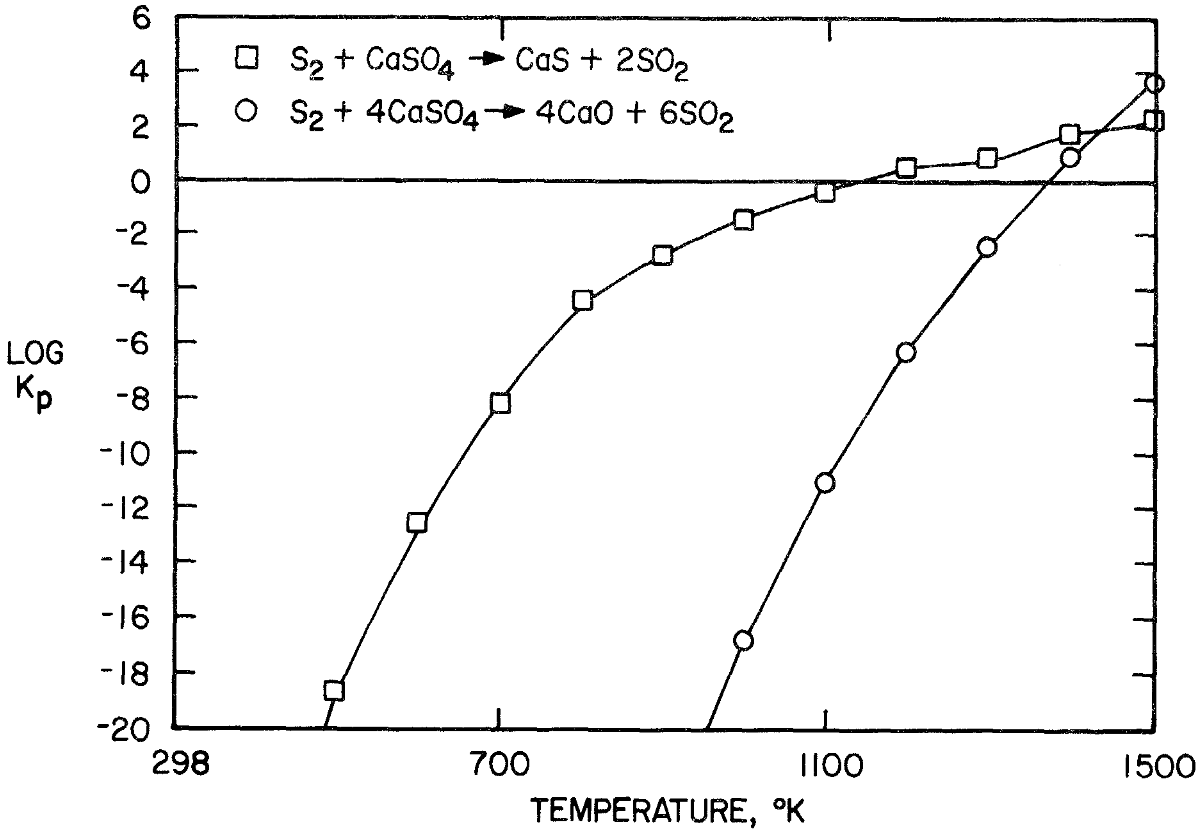

Figure 6. Relationship between reaction temperature and equilibrium constant for equations 35-36.

$$\mathrm{CaO + SO_2 \quad CaSO_3} \tag{37}$$

$$\mathrm{4CaSO_3 \rightarrow 3CaSO_4 + CaS} \tag{38}$$

Therefore, calcium sulfite exists as an unstable intermediate compound which may have little influence on the $CaSO_4$ reduction reactions at high temperature.

Since sulfur was the most desirable final product in our study, an examination of the sulfur reactions with the other reactants described above was investigated. The following reactions were studied:

$$\mathrm{0.5S_2 + O_2 \rightarrow SO_2} \tag{39}$$

$$\mathrm{0.5S_2 + 1.5\ O_2 \rightarrow SO_3} \tag{40}$$

$$\mathrm{0.5S_2 + H_2 \rightarrow H_2S} \tag{41}$$

$$\mathrm{0.5S_2 + C + 0.5\ O_2 \rightarrow COS} \tag{42}$$

$$\mathrm{S_2 + C \rightarrow CS_2} \tag{43}$$

Sulfur is easily oxidized to SO_2 and SO_3 with oxygen (equations 39-40), but the reduction to H_2S by hydrogen (equation 41) was not as favorable. Sulfur can be readily converted to carbon oxysulfide (equation 42), but it is more difficult to convert to CS_2 (equation 43, Figure 7).

Reduction reactions of SO_2 to sulfur by different reducing agents were:

$$\mathrm{SO_2 + 2H_2S \rightarrow 1.5S_2 + 2H_2O} \tag{44}$$

$$\mathrm{SO_2 + C \rightarrow 0.5S_2 + CO_2} \tag{45}$$

$$\mathrm{SO_2 + 2C \rightarrow 0.5S_2 + 2CO} \tag{46}$$

$$\mathrm{SO_2 \quad 2CO \rightarrow 0.5S_2 + 2CO_2} \tag{47}$$

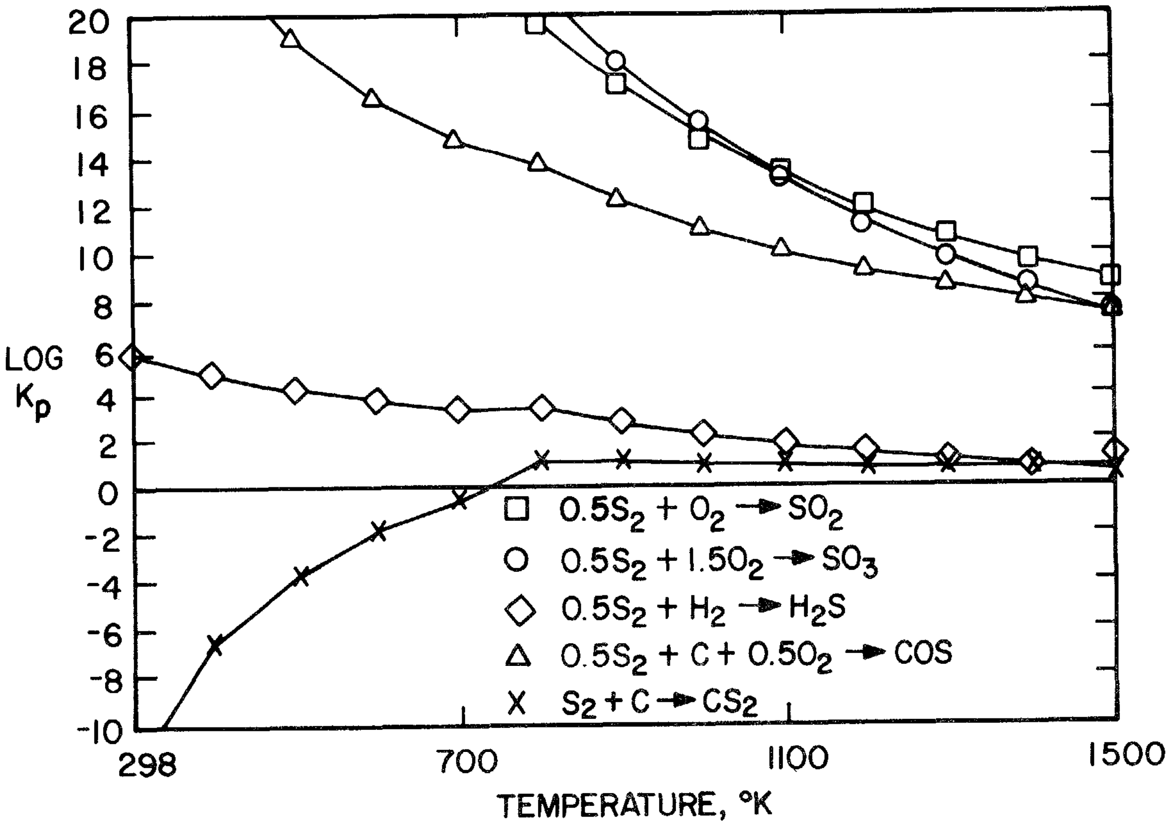

Figure 7. Relationship between reaction temperature and equilibrium constant for equations 39-43.

$$SO_2 + 2H_2 \rightarrow 0.5S_2 + 2H_2O \quad (48)$$

$$SO_2 + H_2 + CO \rightarrow 0.5S_2 + CO_2 + H_2O \quad (49)$$

$$3SO_2 + 2CH_4 \rightarrow 1.5S_2 + 2CO + 4H_2O \quad (50)$$

$$SO_2 + 2COS \rightarrow S_2 + 2CO_2 \quad (51)$$

These reactions were all favorable, as shown in Figures 8-9. Therefore, SO_2 can be converted directly to sulfur if other more favorable reaction routes are not available under the same reaction conditions.

Sulfur dioxide reduction reactions to produce H_2S with different reducing agents were likewise evaluated:

$$SO_2 + 1.5C + H_2O \rightarrow H_2S + 1.5CO_2 \quad (52)$$

$$SO_2 + 3C + H_2O \rightarrow H_2S + 3CO \quad (53)$$

$$SO_2 + 3CO + H_2O \rightarrow H_2S + 3CO_2 \quad (54)$$

$$SO_2 + 3H_2 \rightarrow H_2S + 2H_2O \quad (55)$$

$$SO_2 + 2CO + H_2 \rightarrow H_2S + 2CO \quad (56)$$

$$SO_2 + CH_4 \rightarrow H_2S + CO + H_2O \quad (57)$$

All of these reactions (equations 52-57) were very favorable (Figure 10) and were almost equally effective as the sulfur-forming reactions (equations 44-51). Therefore, the major reaction products from the SO_2 reduction reactions under the same reducing conditions may be a mixture of H_2S and elemental sulfur (equation 48 versus 55, equation 49 versus 56, and equation 50 versus 57). Depending on the specific reducing conditions, either H_2S or elemental sulfur can be the dominant product. When SO_2 is reduced with carbon or CO alone (equations 45-47). the reaction product will be elemental

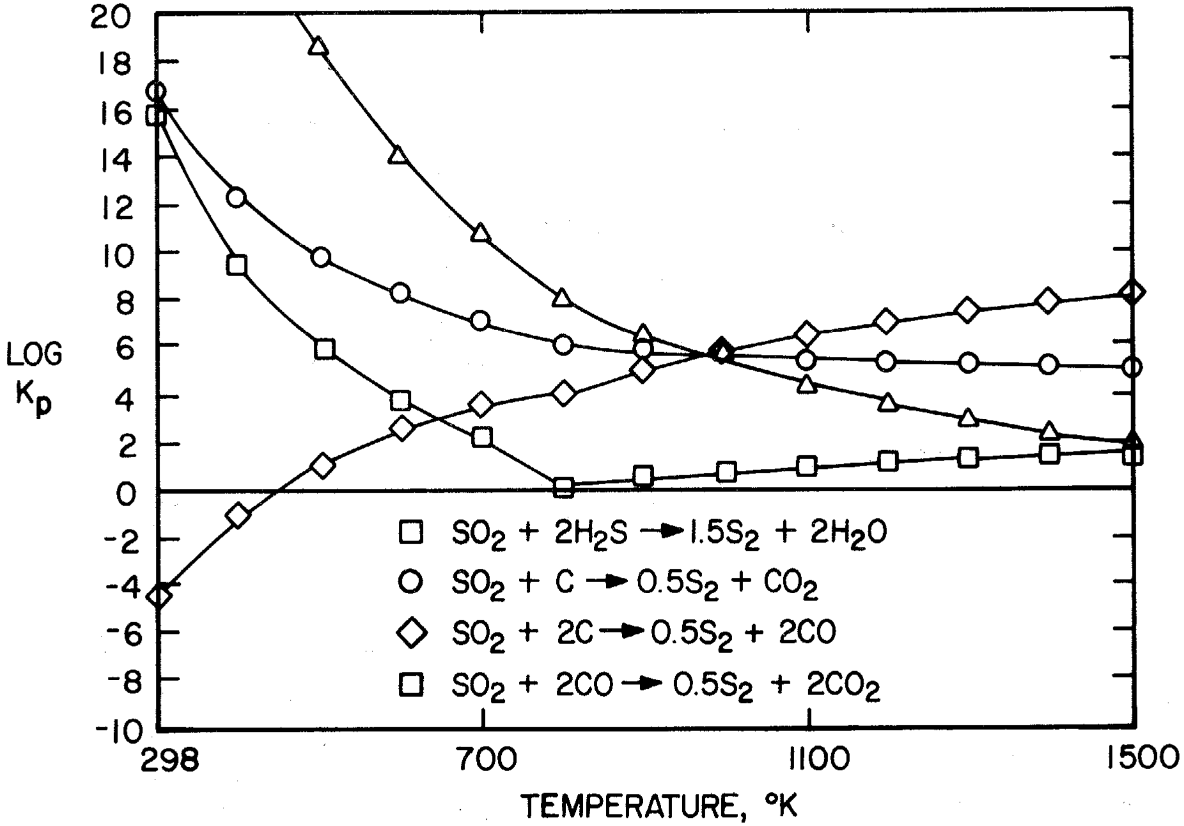

Figure 8. Relationship between reaction temperature and equilibrium constant for equations 44-47.

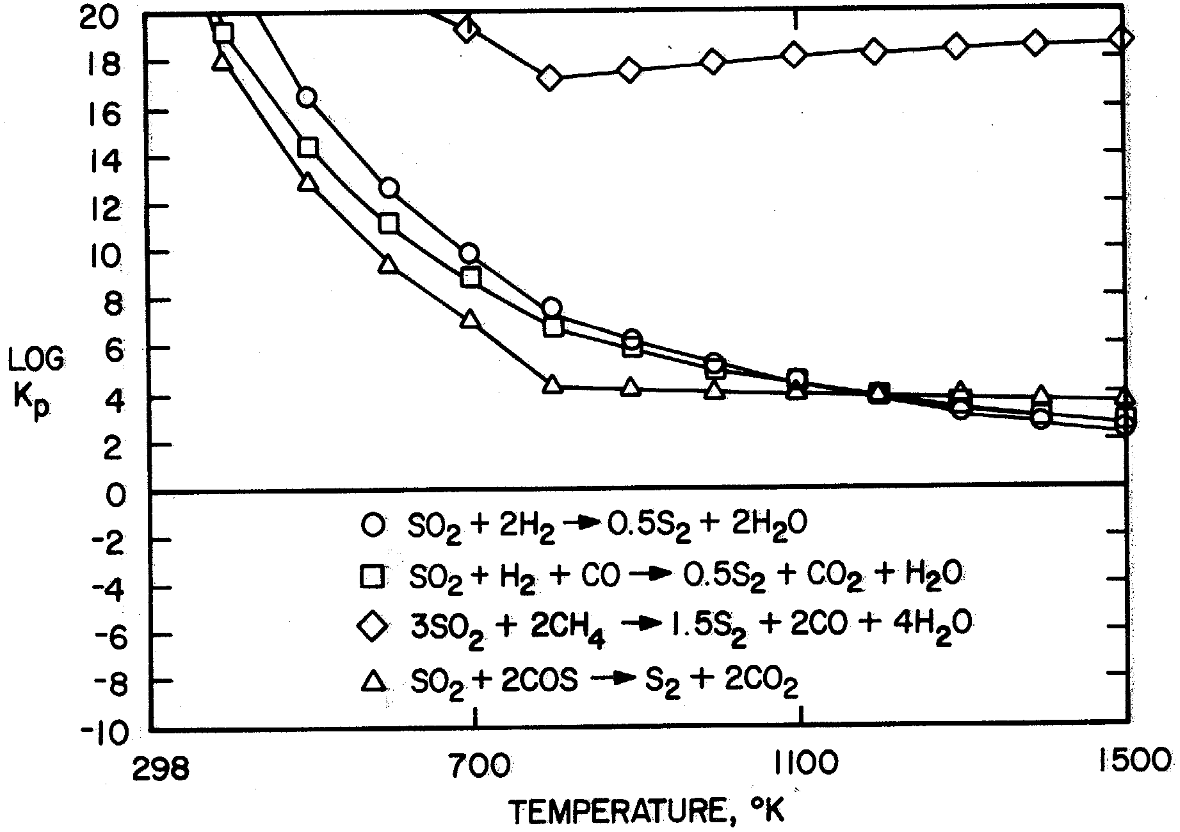

Figure 9. Relationship between reaction temperature and equilibrium constant for equations 48-51.

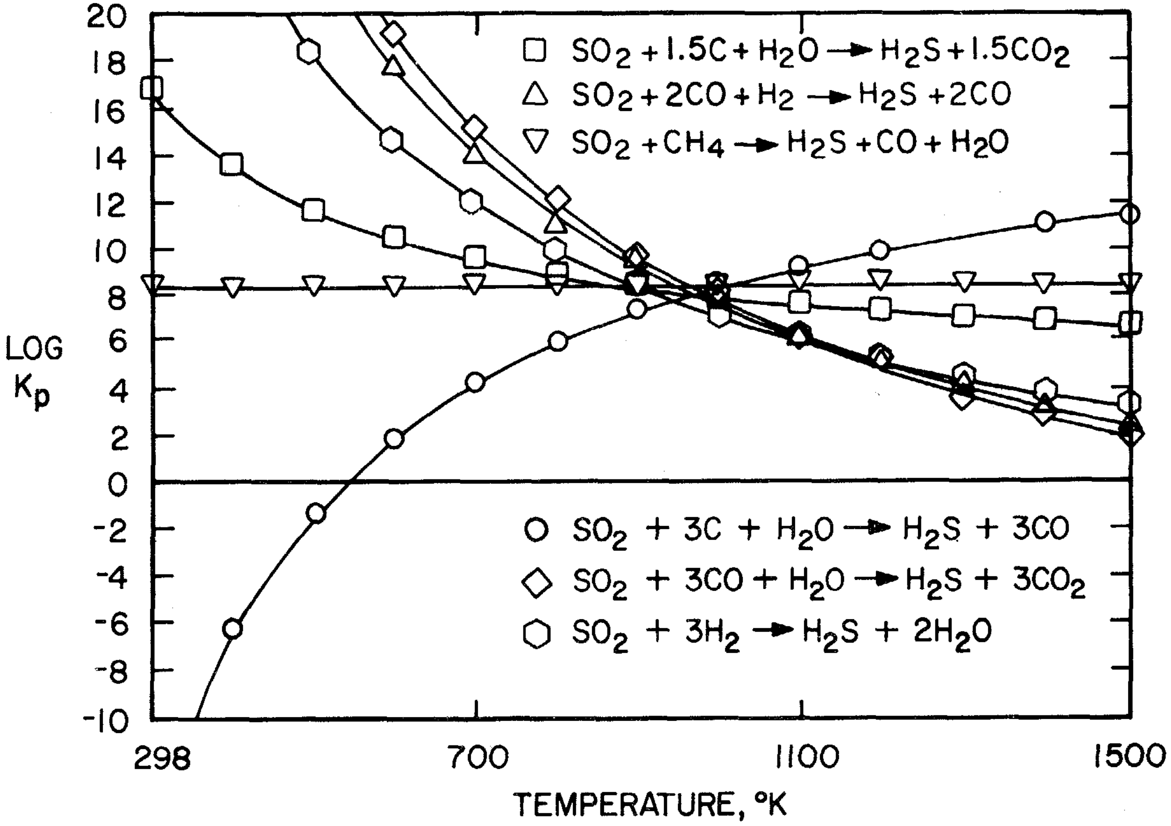

Figure 10. Relationship between reaction temperature and equilibrium constant for equations 52-57.

sulfur; but entrained moisture in the system resulted in the final product being a mixture of H_2S and elemental sulfur (equation 45 versus 52, equation 46 versus 53, and equation 47 versus 54).

The reduction reactions of SO_2 to carbon oxysulfide also were evaluated:

$$SO_2 + C + H_2 \rightarrow COS + H_2O \tag{58}$$

$$SO_2 + CO + 2H_2 \rightarrow COS + 2H_2O \tag{59}$$

$$SO_2 + CH_4 + 0.5\ O_2 \rightarrow COS + 2H_2O \tag{60}$$

$$SO_2 + 2C \rightarrow COS + CO \tag{61}$$

All four reduction reactions (equations 58-61) were favorable routes to produce COS, as shown in Figure 11. The addition of oxygen in the system (equation 60) increased the $\underline{K}_p$ value tremendously; therefore, even small amounts of oxygen contamination in the reducing gas stream will favor the formation of COS.

Carbon disulfide formations from SO_2 were evaluated:

$$2SO_2 + 3C \rightarrow CS_2 + 2CO_2 \tag{62}$$

$$2SO_2 + 5C \rightarrow CS_2 + 4CO \tag{63}$$

$$2SO_2 + 6CO \rightarrow CS_2 + 5CO_2 \tag{64}$$

$$2SO_2 + CO + 5H_2 \rightarrow CS_2 + 5H_2O \tag{65}$$

$$2SO_2 + CH_4 + 2H_2 \rightarrow CS_2 + 4H_2O \tag{66}$$

$$2SO_2 + 2CH_4 \rightarrow CS_2 + 3H_2O + CO + H_2 \tag{67}$$

All of these reactions (equations 62-67) were thermodynamically favorable (Figure 12). A comparison between carbon disulfide and carbon oxysulfide

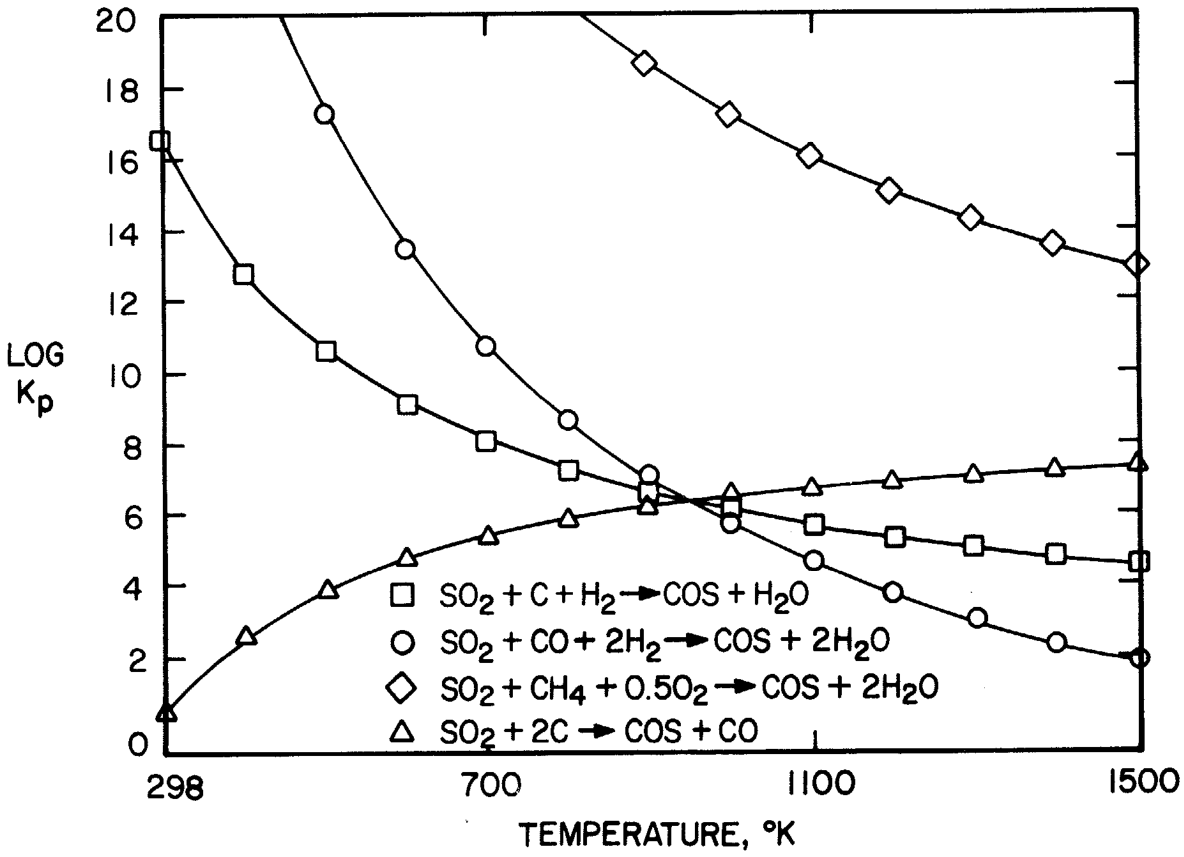

Figure 11. Relationship between reaction temperature and equilibrium constant for equations 58-61.

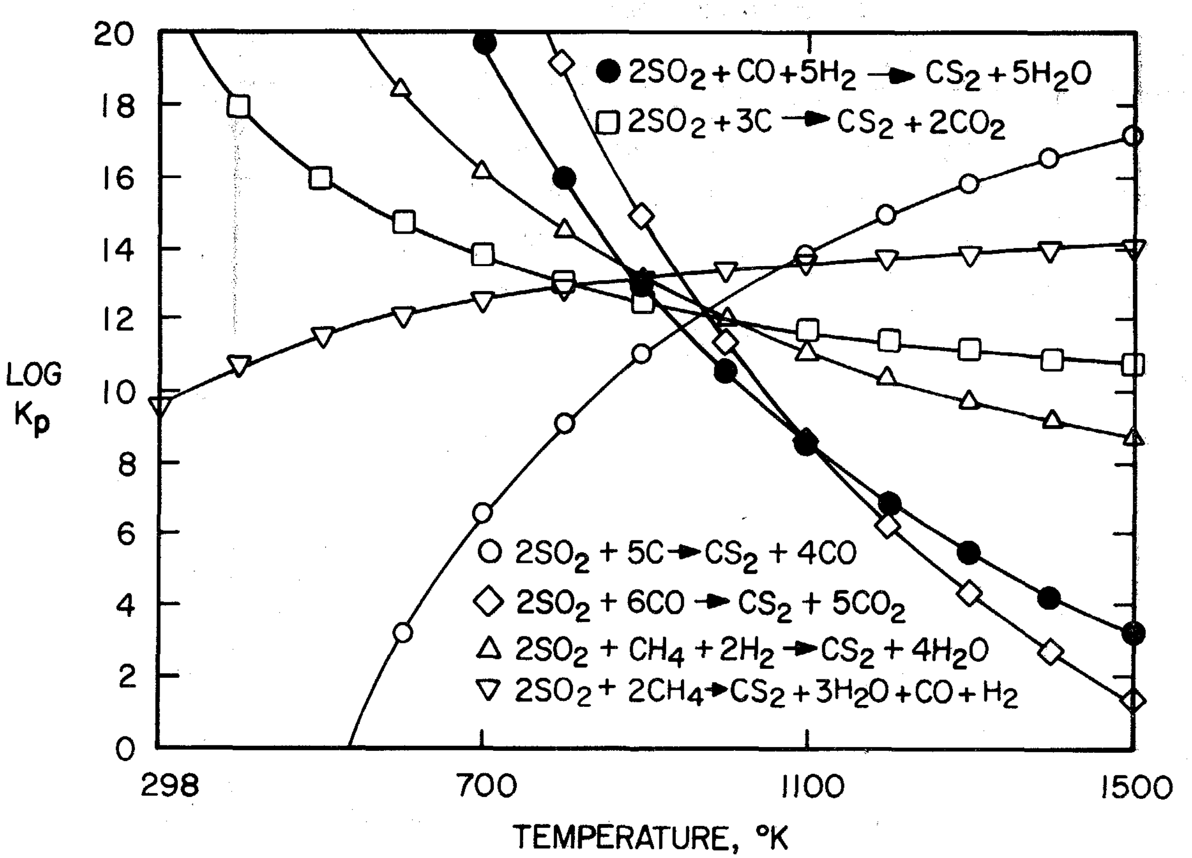

Figure 12. Relationship between reaction temperature and equilibrium constant for equations 62-67.

formation (equation 59 versus 65 and equation 61 versus 63) revealed that the value of these reactions under the same reducing conditions was very close, indicating that a mixture of COS and CS_2 will be produced.

Hydrogen sulfide conversion to elemental sulfur, carbon oxysulfide, and carbon disulfide were studied according to the following reactions:

$$H_2S + CO_2 \rightarrow S_2 + CO + H_2O \qquad (68)$$

$$H_2S + COS \rightarrow S_2 + CO + H_2 \qquad (69)$$

$$H_2S + CO_2 \rightarrow COS + H_2O \qquad (70)$$

$$2H_2S \quad CO_2 \rightarrow CS_2 + 2H_2O \qquad (71)$$

$$2H_2S + C + O_2 \rightarrow CS_2 + 2H_2O \qquad (72)$$

$$2H_2S \quad CO + 0.5\ O_2 \rightarrow CS_2 + 2H_2O \qquad (73)$$

$$2H_2S + CH_4 + 4O_2 \rightarrow CS_2 + 4H_2O \qquad (74)$$

As shown in Figures 13-14, the conversion of H_2S to elemental sulfur, COS, or CS_2 was very difficult (equations 68-71) at low temperatures. Conversely, these data indicated that S, COS, or CS_2 can be converted easily to H_2S, which is the reverse reaction of equations 68-71. An addition of oxygen (equations 72-74) with reducing agents such as CO and CH_4 may readily convert H_2S to CS_2.

Elemental sulfur conversion to carbon oxysulfide or carbon disulfide was studied according to the following reactions:

$$0.5S_2 + CO \rightarrow COS \qquad (75)$$

$$0.5S_2 + CO_2 + H_2 \rightarrow COS + H_2O \qquad (76)$$

$$0.5S_2 + CH_4 + 1.5\ O_2 \rightarrow COS + 2H_2O \qquad (77)$$

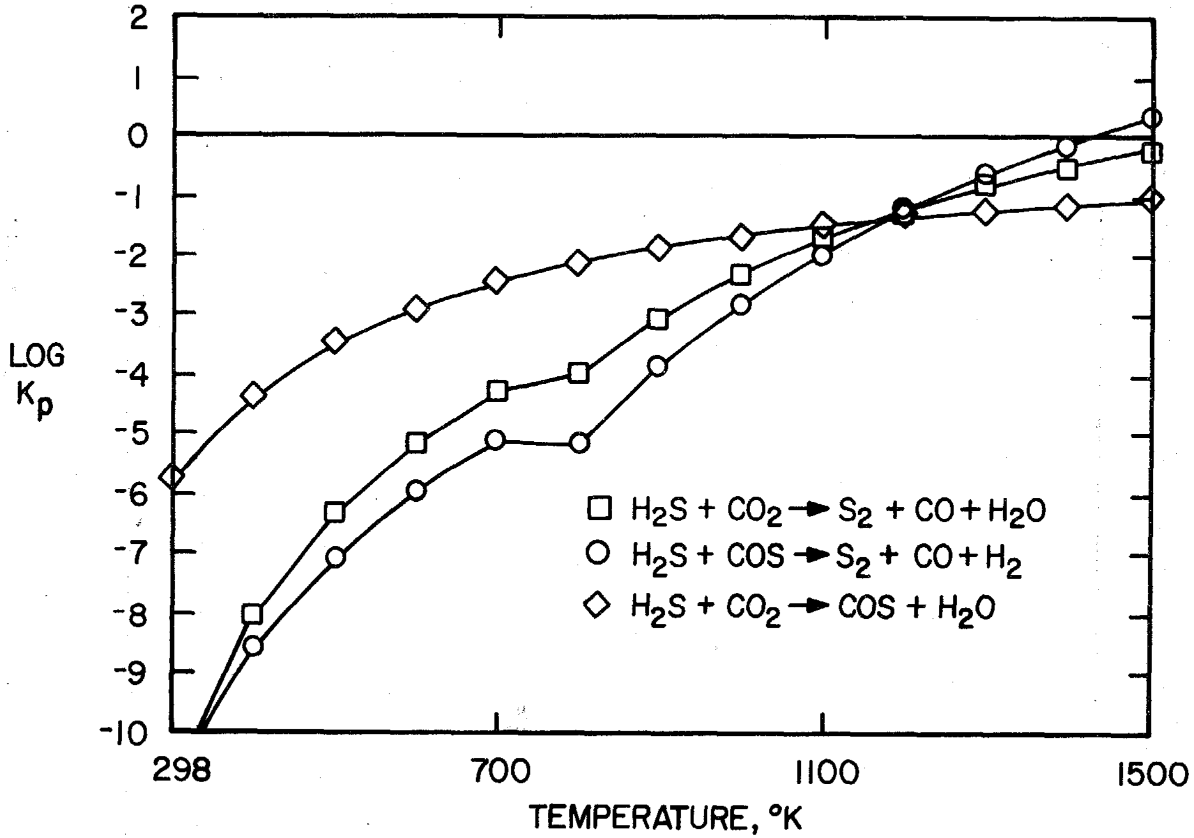

Figure 13. Relationship between reaction temperature and equilibrium constant for equations 68-70.

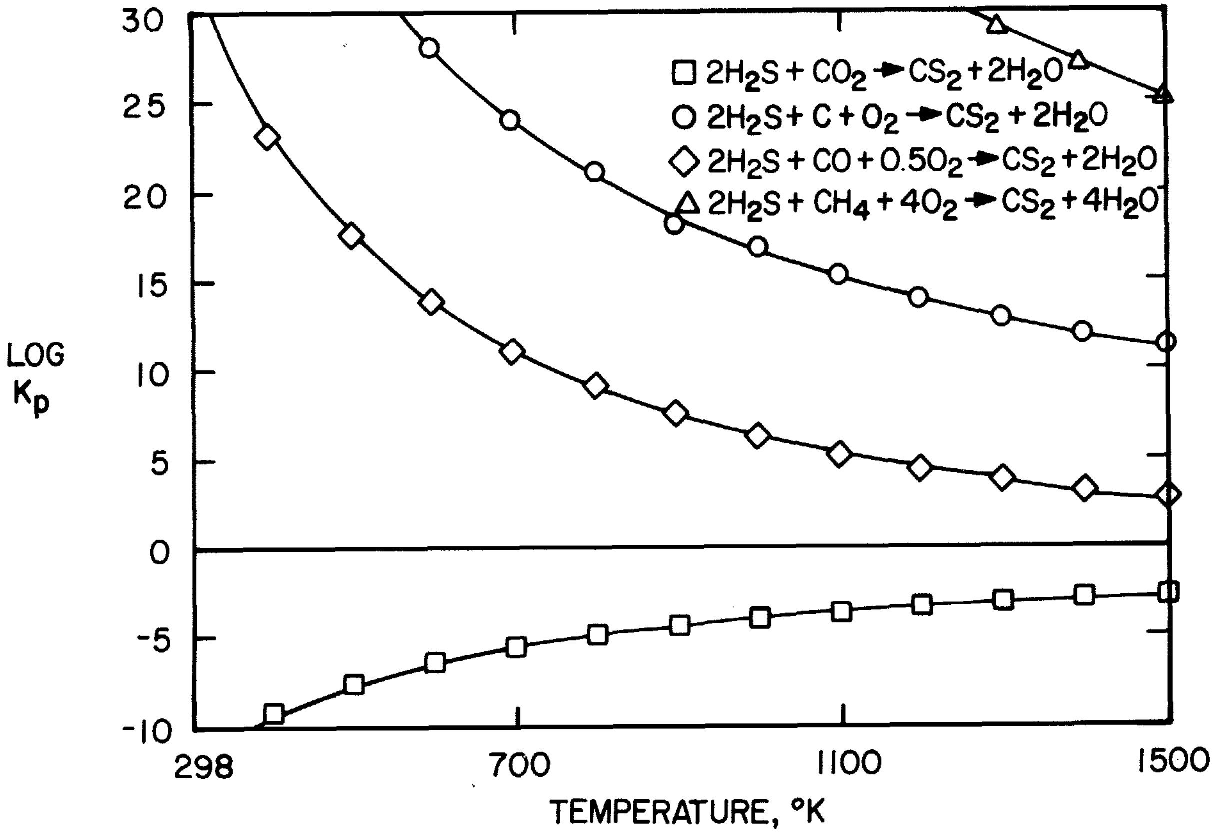

Figure 14. Relationship between reaction temperature and equilibrium constant for equations 71-74.

$$S_2 + CO + H_2 \rightarrow CS_2 + H_2O \qquad (78)$$

$$S_2 + CH_4 + O_2 \rightarrow CS_2 + 2H_2O \qquad (79)$$

At equilibrium, elemental sulfur may coexist with carbon oxysulfide (equations 75-76, Figure 15) or carbon disulfide (equation 78) since their $\underline{K}_{\underline{p}}$ values are near zero (Figure 16). When oxygen is introduced in the system (equations 77 and 79). the sulfur will be converted completely to either COS or CS_2.

Finally, the conversion of carbon oxysulfide to carbon disulfide was explored by the following reactions:

$$2COS + C \rightarrow CS_2 + 2CO \qquad (80)$$

$$2COS + H_2 \rightarrow CS_2 + CO + H_2O \qquad (81)$$

$$2COS + CH_4 + O_2 \rightarrow CS_2 + 2CO + 2H_2O \qquad (82)$$

Some fractions of carbon oxysulfide will be converted to carbon disulfide under these reducing conditions (equations 80-81), and the degree of conversion depends on the reaction conditions and reducing agent. Therefore, the probability of COS and CS_2 coexisting at equilibrium is very large under these reducing conditions. This same conclusion also is supported by the evidence presented previously in the discussion of equation 59 versus 65 and equation 61 versus 63. However, the presence of oxygen in the system (equation 82) makes the COS conversion to CS_2 almost complete. The addition of excess oxygen, as demonstrated in equations 71-74, 78-79, and 80-82, will result in further oxidation of CS_2 to SO_2 and is one of the most favorable reactions (Figure 16):

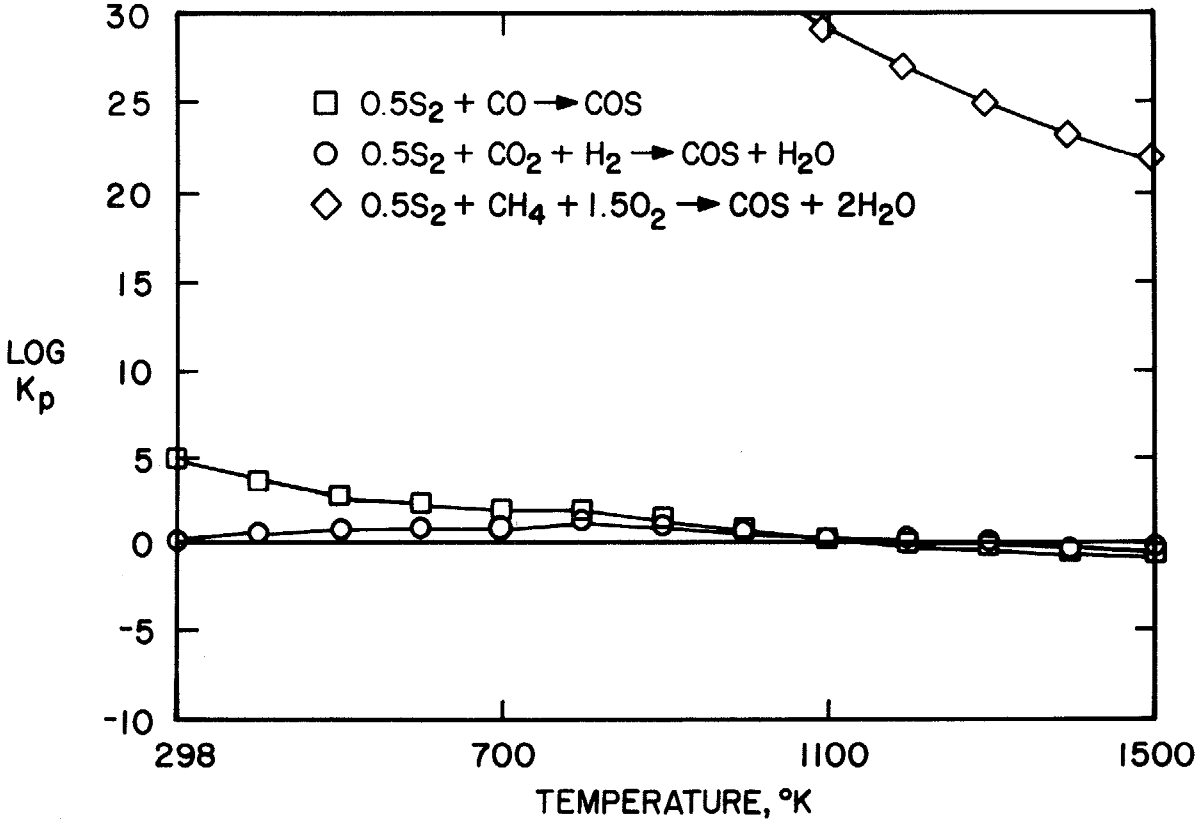

Figure 15. Relationship between reaction temperature and equilibrium constant for equations 75-77.

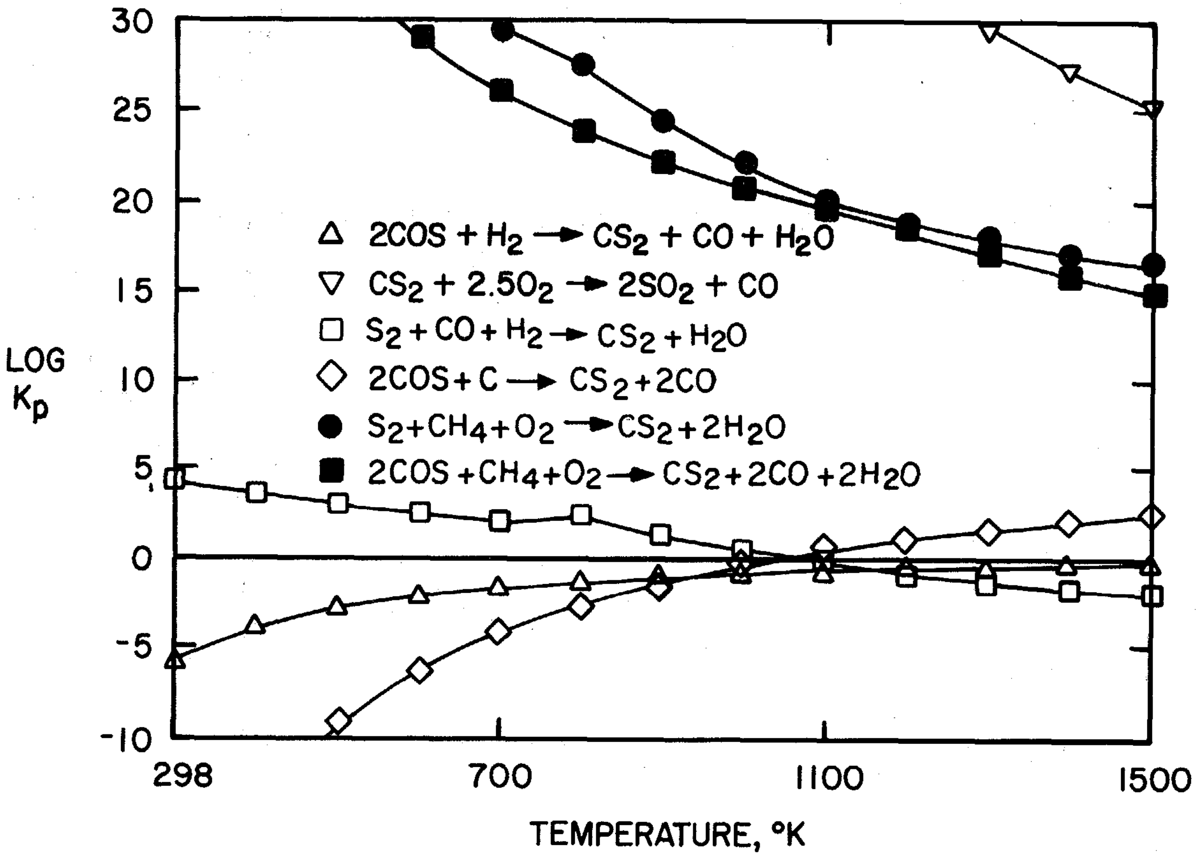

Figure 16. Relationship between reaction temperature and equilibrium constant for equations 78-83.

$$CS_2 + 2.5\ O_2 \rightarrow 2SO_2 + CO \qquad (83)$$

CONCLUSIONS

The regeneration of CaO from $CaSO_4$ product generated from the gas desulfidization processes using limestone scrubbing or phosphogypsum is feasible. This can be accomplished by a reductive decomposition to produce CaO and SO_2, as indicated by equations 18-23. The reducing agents are carbon or carbon-derived compounds, such as CO and H_2. Calcium oxide will be recycled to absorb SO_2 from flue gases or used as a component for cement production. Sulfur dioxide will be sent for H_2SO_4 production or reduced to H_2S by equations 52-57 and subsequently converted to elemental sulfur by the well-known Claus process (equation 44). This sulfur conversion process is slightly unattractive because of high energy requirements and extensive capital investment. A better alternative for converting SO_2 to elemental sulfur is the direct conversion reactions depicted by equations 45-47. These reactions may occur in a column of carbon at lower temperatures as SO_2 gas is passed through the column. Exit gases may contain S_2, unreacted SO_2, and other by-products (such as CS_2, COS, and CO). The elemental sulfur can be preferentially separated by condensation, and the remaining exit gas can be oxidized to SO_2 and recycled for further sulfur recovery. Another possible direct thermal decomposition to elemental sulfur is a one-step process where the mixture of carbon and $CaSO_4$ reacts with steam or another reaction medium. This reaction scheme is favored by thermochemical evaluation.

These direct conversion processes require less energy input and less capital expenditure than the H_2S route (equations 52-57). However, there are only limited data available on this direct process (Fleck, 1952; Lind, 1973). The reaction conditions (such as temperature, pressure, residence time, SO_2 concentration, carbon column length, type of carbon, and other unknown conditions) will affect the reaction velocity, as well as the distribution of the sulfur species in the exit gas. A detailed study on this process by a laboratory-scale experiment is warranted. A further consideration of the whole regeneration system is shown in Figure 17.

Alternately, $CaSO_4$ regeneration can be effectively carried out by a reductive decomposition to produce CaS at lower temperatures (equations 24-26). The intermediate product, CaS, then is reacted with steam in the presence of carbon to produce H_2S and CaO according to the simultaneous reactions of equations 15, 16, and 34. This H_2S conversion step has not been thoroughly studied; different reaction conditions will influence the reaction kinetics, as well as the conversion efficiency. If the proper combination of reaction conditions to convert CaS to H_2S in a laboratory study is determined, the equipment needed for this process will be a two-section rotary kiln where the CaS conversion reaction takes place in the first section and H_2S conversion occurs with steam introduction in the second section.

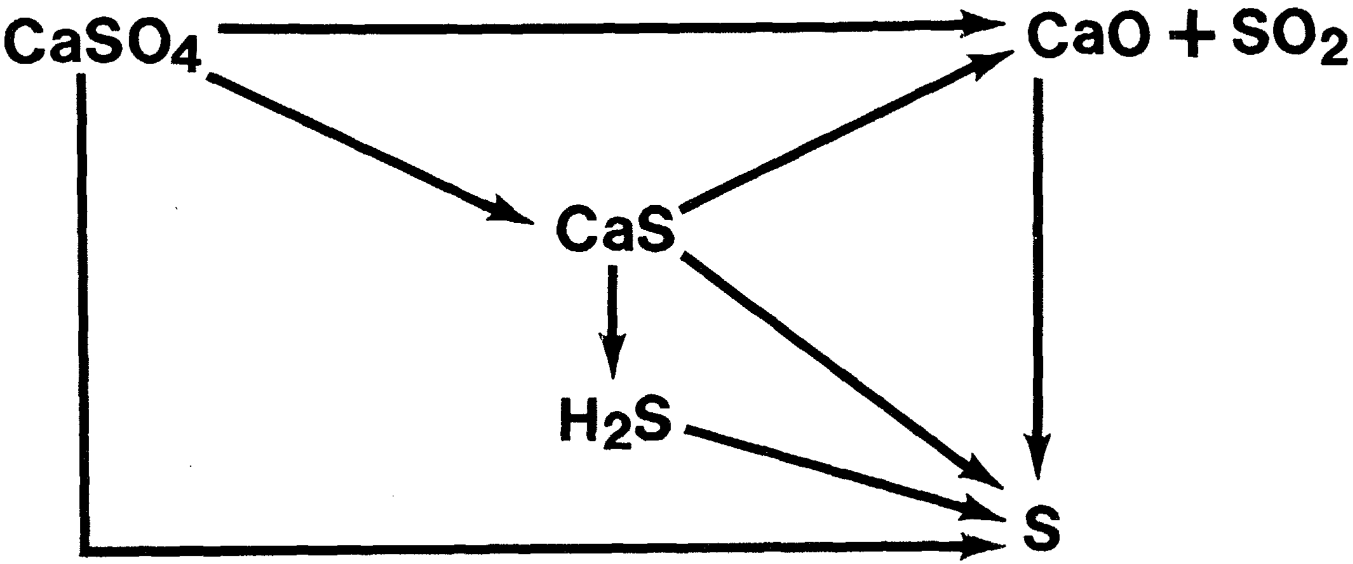

Figure 17. Regeneration system.

Figure 1. Relationship between reaction temperature and equilibrium constant for equations 15-19.

Figure 2. Relationship between reaction temperature and equilibrium constant for equations 20-23.

Figure 3. Relationship between reaction temperature and equilibrium constant for equations 18-2, 21-2, and 22-2.

Figure 4. Relationship between reaction temperature and equilibrium constant for equations 24-28.

Figure 5. Relationship between reaction temperature and equilibrium constant for equations 29-34.

Figure 6. Relationship between reaction temperature and equilibrium constant for equations 35-36.

Figure 7. Relationship between reaction temperature and equilibrium constant for equations 39-43.

Figure 8. Relationship between reaction temperature and equilibrium constant for equations 44-47.

Figure 9. Relationship between reaction temperature and equilibrium constant for equations 48-51.

Figure 10. Relationship between reaction temperature and equilibrium constant for equations 52-57.

Figure 11. Relationship between reaction temperature and equilibrium constant for equations 58-61.

Figure 12. Relationship between reaction temperature and equilibrium constant for equations 62-67.

Figure 13. Relationship between, reaction temperature and equilibrium constant for equations 68-70.

Figure 14. Relationship between reaction temperature and equilibrium constant for equations 71-74.

Figure 15. Relationship between reaction temperature and equilibrium constant for equations 75-77.

Figure 16. Relationship between reaction temperature and equilibrium constant for equations 78-83.

Figure 17. Regeneration system.

REFERENCES

Biswas, S. C., V. P. Sabharwal, and B. K. Dutta. 1971. Sulfur from gypsum: reduction of gypsum to calcium sulphide. Technology. 8: 58-60.

Curran, G. P., B. Pasek, M. Pell, and E. Gorin. 1973. Low-sulfur producer gas via an improved fluid-bed gasification process. Proceedings of Third International Conference on Fluidized-Bed Combustion. Report No. EPA--650/2-73-053. December 1973: III-6-1 through III-6-17.

Duda, W. H. 1966. Simultaneous production of cement clinker and sulfuric acid. Min. Proc. August 1966: 10-26.

Farooqi, R., Y. Venkatesham, and D. S. Datar. 1961. Sulfur from gypsum: part I--production of hydrogen sulphide from gypsum. J. Sci. Industr. Res. 20D: 36-39.

Fleck, A. 1952. The British sulphuric acid industry---a retrospect and a research prospect. Chem. Indus. December 6, 1952: 1184-1193.

Foerster, F. and K. Kubel. 1924. Contributions to the knowledge of sulfurous acids and its salts. Z. anorg. allg. chem. 139: 261-292.

Ginstling, A. M. and A. D. Volkov. 1960. Reactions of elemental sulfur formation in the interaction of calcium sulfate with carbon. Zh. Prikl. Khim. 33: 1700-1704.

Gorin, E. 1973. Conversion of calcium sulfate to calcium oxide and elemental sulfur. U.S. Patent No. 3,729,551.

Hull, W. Q., F. Schon, and H. Zirngibl. 1957. Sulfuric acid from anhydrite. Ind. Eng. Chem. 49: 1204-1214.

Lind, W. H. 1973. Conversion of metal sulfates to sulfur and substantially sulfide--free solid. U.S. Patent No. 3,726,957.

Lloyd, M., J. H. Marten, and T. J. Kendron. 1985. Phosphogypsum: a source of sulfur dioxide. Paper presented at the American Chemical Society meeting, Chicago, Illinois, September 1985.

Lowell, P. S. and K. Schwitzgebel. 1969. Thermochemistry of the calcium-sulfur-oxygen system and interpretation of the decomposition behavior of $CaSO_3$. Technical Memorandum 004-009-Ch21. Austin, Texas: Tracor.

Pearson, M. J. 1973, Developments in claus catalysts. Hydrocarbon Processing. February 1973: 81-85.

Pecshkovskii, V. V. and T. G. Mel'tseva. 1964. The interaction between calcium oxide and sulfur dioxide under reducing conditions. Zh. PrikL. Khim. 37: 240-246.

Salladay, D. G., D. E. Nichols, J. T. Berry, D. B. Call, E. A. Harre, and Y. K. Kim. 1986. AFBC waste utilization plan. Internal TVA report.

Schenck, R. and K. Jordan. 1929. Equilibrium studies concerning the system calcium-sulfur-oxygen. Z. anorg. allg. Chem. 178: 389-399.

Schenck, R. and K. Jordan. 1933. Equilibrium studies concerning the system calcium-sulfur-oxygen. Z. anorg. allg. Chem. 310: 305-312.

Shepard, M. 1985. Managing the by-products of coal combustion. EPRI Journal. October 1985: 21-35.

Skopp, A., J. T. Sears, and R. R. Bertrand. 1969. Fluid-bed studies of the limestone based flue-gas desulfurization process. Report No. GR-9-FGS-69. Exxon Research and Engineering Company, Government Research Division.

Slack, A. V. 1968. Phosphoric acid. Part II. New York: Marcel Dekker, Inc., pp 503-577.

Smith, D. J. 1985. Advances in fluidized bed combustion and cogeneration. Power Engineering. October 1985: 26-32.

Stull, D. R. and H. Prophet. 1971. JANAF thermochemical tables. 2nd ed. U.S. Department of Commerce, National Bureau of Standards. 197.5, 1978, and 1982 supplements.

Swift, W. M., A. F. Panek, G. W. Smith, G. J. Vogel, and A. A. Jonke. 1976. Decomposition of calcium sulfate: a review of the literature. Report No. ANL-76-122. Argonne, Illinois: Argonne National Laboratory.

Swift, W. M. and T. D. Wheelock. 1975. Decomposition of calcium sulfate in a two-zone reactor. Ind. Eng. Chem. Proc. Des. Dev. 14: 323-327.

Turkdogan, E. T. and J. V. Vinters. 1976. Reduction of calcium sulphate by carbon. Inst. Min. Metall. September 1976: C117-123.

United Nations Industrial Development Organization. 1971. The manufacture of cement and sulphuric acid from calcium sulphate. New York: United Nations.

Vogel, G. J., E. L. Carls, J. Ackerman, M. Haas, J. Riha, C. B. Schoffstoll, J. Hepperly, and A. A. Jonke. 1973. Reduction of atmospheric pollu--tion by the application of fluidized-bed combustion and regeneration of sulfurcontaining additives. Argonne, Illinois: Argonne National Laboratory Annual Report, July 1972-June 1973, Report No. ANL/ES-CEN-1005.

Wagman, D. D., W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttall. 1982. The NBS tables of chemical thermodynamic properties. Selected values for inorganic and C_1 and C_2 organic substances in SI units. J. Phys. Chem. Ref. Data. 11: supplement No. 2, 392 pp.

Wheelock, T. D. 1958. Desulfurization of gypsum. Ph.D. thesis. Ames, Iowa: Iowa State University of Science and Technology.

Wheelock, T. D. and D. R. Boylan. 1960. Reduction decomposition of gypsum by carbon monoxide. Ind. Eng. Chem. 52: 215-217.

Wheelock, T. D. and D. R. Boylan. 1968. Sulfuric acid from calcium sulfate. Chem. Eng. Prog. 64: 87-92.

Zadick, T. W., R. Zavaleta, and F. P. McCandless. 1972. Catalytic reduction of calcium sulfate to calcium sulfide with carbon monoxide. Ind. Eng. Chem. Proc. Des. Dev. 11: 283-287.

Zawadzki, J. 1932. The system calcium-sulfur-oxygen. Z. anorg. allg. chem. 205: 180-190.

CONTROL OF PHOSPHOGYPSUM QUALITY TO MEET VARIOUS APPLICATIONS IN HEMI-DI PROCESS

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ABSTRACT

There is a general tendency that phosphogypsum from hemi-dihydrate strong acid process is agglomerated. The agglomerated gypsum is hard and easy to filter and, when it is used in various applications, especially in gypsum board production, it has advantages such as less moisture content after centrifuge, higher tensile strength of final product, etc., but also a disadvantage of longer setting time in board production. In order to produce gypsum board in the same production rate with the same plant using such gypsum, it is required to change the setting time by controlling the degree of agglomeration by way of changing operation condition of phosphoric acid plant.

It was found that agglomerated crystals were formed when both aluminium and fluorine ion content in liquid in which hemi-hydrate crystal was recrystallized to dihydrate were high and aluminium ion was accumulated in this liquid in case of this phosphoric acid process.

It is difficult to reduce aluminium ion content in liquid but fluorine ion can be reduced by adding active silica to liquid and making fluorine evolved as fluosilicic acid. In our factory, we are operating the phosphoric acid plant to obtain gypsum of proper agglomeration by controlling the silica addition.

1. EXPLANATION OF FLOW OF HEMI-DI PROCESS

There are two kinds of hemi-dihydrate phosphoric acid manufacturing process, one is to produce 30 % P_2O_5 product acid with one filter and the other is to produce 40 - 50 % acid without concentration procedure using two filters. The process taken up here is the latter one, strong acid process with two filters.

The flow of this process is given in attached drawing. The process is split into two sections, digestion section and hydration section and digester section needs two digesters. Return acid, recycle slurry, a part of sulphuric acid and phosphate rock are charged to No.1 digester. The rock used here can be coarse rock of less than 2 mm in particle size. Some phosphate rock can be directly used without grinding but in most cases the rock is screened at first and only over screen is ground. The saving of electricity for ginding is fairly big.

The reaction temperature of both No.1 and No.2 digesters are 90 - 100 °C. No.1 digester is kept at the condition of no free sulphuric acid and here phosphate rock is dissolved into the acid. The slurry in No.1 digester overflows into No.2 digester, sufficient sulphuric acid is added here and large and easy-to-filter hemihydrate crystal is obtained. Slurry in No.2 digester is pumped up to vacuum cooler and cooled slurry partly goes back to digester and partly charged to hemi-filter.

The first filtrate of hemi-filter is the product acid. Its strength is 40 -50 % P_2O_5 and it is decided from water balance of raw material sulphuric acid and moisture in phosphate rock or requirement of the application for fertilizer. The cake is further washed by the first filtrate of di-filter and this filtrate becomes return acid mixed with a part of the product acid.

The washed cake is repulped by the second filtrate of di-filter and goes to hydration tank. Here under the condition of 10 - 15 % P_2O_5 and 50 - 65 °C, hemihydrate is recrystallized to dihydrate and undecomposed rock in hemihydrate cake is further decomposed by added sulphuric acid. This dihydrate slurry is filtered at di-filter and gypsum cake is washed by water.

2. ACCUMULATION OF ALUMINIUM

As can be understood from the explanation of the flow, the liquid in hydration section comes back to digestion section as cake washing acid and this may cause accumulation of a certain impurities in the system and it is the most remarkably observed with aluminium. The solubility of aluminum in high concentration acid of digesters is small and solid aluminium compounds go to hydration section together with hemihydrate cake. In hydration section where the acid concentration is low, the aluminium compound is dissolved into liquid phase and a part of this liquid comes back to digestion section as washing acid of hemihydrate cake.

In such way, aluminium is recycled between hydration section and digestion section and accumulated in hydration section. As a result, aluminium content both in hydration liquid and discharged gypsum are higher than those in other processes. This is the special point regarding gypsum quality of hemi-dihydrate two stage filtration process.

3. REQUIRED GYPSUM QUALITY

When gypsum is used for various applications, required gypsum qualities are different for each application and each step. As examples of gypsum application, following four are chosen and required qualities are discussed.

Gypsum board
Plaster
Cement retarder
Sulphuric acid and cement

3.1 GYPSUM BOARD

Gypsum board is produced in the following way. At first gypsum is dewatered by centrifuge and then dried and calcined either by fire or steam. In these steps, gypsum of good dewatering nature, that is, large, uniform and ball type crystal and not needle type is preferred. Next step is grinding and for this step soft and fine crystal is preferred opposite to previous step. Then comes to the step of the slurry preparation in which the most important characteristic is to give fluidity of slurry with less water content, so called lower water consistency. To give this lower water consistency, again ball type crystal is preferred.

The prepared slurry is poured on the paper moving on the belt conveyor, the paper is put also on the other surface and the gypsum is hardened by hydration. Here faster setting time is required and soft and fine crystal shows faster setting time. Formed board is cut in size and dried in dryer. In these sections, crystal of low water consistency is preferred with less energy consumption for drying and higher strength of the final product.

3.2 PLASTER

The plaster production process is similar to up to grinding section of gypsum board production process.

As can be seen from these explanations, in gypsum board or plaster production, two characteristics contrasting each other are required in one manufacturing process and it is advisable to procure gypsum of intermediate characteristic between the two in order to achieve the best economy in production.

3.3 CEMENT RETARDER

Gypsum is added in cement as retarder and its content is about 3 - 4 % in cement. For this application, it used to be required that the gypsum is granulated in 10 - 20 mm ball after mixing lime. But these days, phosphogypsum from phosphoric acid plant is directly used in cement plant for the economy of cement production.

In this case, watersoluble acidic material such as phosphoric acid, sulphuric acid, hydrofluoric acid, fluorosilicic acid, etc., gives bad effect in making the setting time of cement longer. In order to neutralize such materials, powder lime is generally mixed with gypsum.

But basically these material can be removed by water washing and ball type gypsum crystal is preferred for this purpose, because such crystal shows better dewatering characteristic.

3.4 SULPHURIC ACID AND CEMENT

There are only two or three commercial plants to produce sulphuric acid and cement from gypsum in the world, but there exists the possibility of increase if today's high sulphur price situation continues. For this application, it is reported that P_2O_5 content in gypsum must be less than 0.5 % and F content must be less than 0.15 %. High P_2O_5 content gives bad effect in product cement quality and fluorine gives bad effect both for cement production and for sulphuric acid catalyst.

In hemi-dihydrate process, P_2O_5 content in gypsum seldom exceeds 0.5 %, but F content differs depending on the nature of raw material phosphate rock. Nevertheless it is possible to control F content in gypsum in similar way to crystal type control.

4. GYPSUM FROM HEMI-DI PROCESS

Various crystal type of gypsum is obtained in hemi-dihydrate process and the type is influenced by raw material phosphate rock, operation condition, etc. But crystal type is roughly classified into agglomerated crystal and single crystal. Naturally the crystal of intermediate nature also exists.

Agglomerated one is ball type with average diameter of 100 micron. As the size is rather big and uniform, the moisture content after centrifuge can be less than that with other type of crystal. The crystal is hard and needs bigger powder for grinding but the strength of moulded product is higher.

Single crystal is rather soft and a little smaller than the agglomerated one though it is difficult to mention the average diameter for crystal type of needle, rhombic, etc.

To show the difference of nature for crystal types in figure, specific surface area of crystal which is related with the size of crystal, moisture contentafter centrifuge, water consistency at the time of repulping for moulding, setting time for moulding and tensile strength of the moulded product are given in Table I as reference for agglomerated crystal, intermediate one and single crystal.

Table I. Nature of Various Crystals

Crystal	Agglomerated	Middle	Single
Specific surface area (cm^2/g)	1,000	1,500	2,000
Moisture (%)	10	11	12
Consistency (water %)	65	72	80
Final setting time (min.)	90	25	15
Tensile strength (kg/cm^2)	16	15	14

From Table I, it is observed that the agglomerated crystal shows fairly long setting time for moulding and it is necessary to make this setting time shorter to produce moulded products keeping similar productivity to other crystals.

5. FACTORS TO INFLUENCE THE CRYSTAL TYPE

Through the operation of our commercial plant, we found that following three factors in hydration tank liquid were giving influence to make the crystal form agglomerated.

High aluminium content
High fluorine ion content
Low free sulphuric acid content

It is estimated that aluminium is involved in gypsum crystal in the form of aluminium fluoride complex and when such complex is involved in crystal, it tends to be aggromerated, though the reason why the involvement of aluminium fluoride complex in crystal gives the tendency of agglomeration.

As explained in Chapter 2, in hemi-dihydrate process, aluminium tends to accumulate in hydration tank liquid and this is the reason why agglomerated gypsum crystal is obtained in this process. But as aluminium is involved in crystal in the form of aluminium fluoride complex, when fluorine ion content is less in liquid even if aluminium content is high, gypsum crystal shows tendency of less agglomeration.

Table II. Influence of Aluminium and Fluorine on Crystal

(5 % H_2SO_4 in liquid)

Al_2O_3 in liquid (%)	0.5	1.2	1.2
F^- in liquid (%)	0.3	0.2	0.1
Al_2O_3 in gypsum (%)	0.1	0.1	0.1
Specific surface area (cm^2/g)	1,100	1,200	1,500

Table II shows one example of influence of aluminium and fluorine content in liquid on specific surface area which represents agglomeration. When specific surface area is smaller, the crystal is more agglomerated. For the same aluminium content, when fluorine content is less, specific surface area of gypsum is larger, that is, less agglomerated. Even if aluminium content in liquid is less, when fluorine content is high, gypsum is more agglomerated.

Table III. Influence of H_2SO_4 on Crystal

(Al_2O_3 0.8 %, F^- 0.9 % in liquid)

H_2SO_4 in liquid (%)	3	5	8
Al_2O_3 in gypsum (%)	0.3	0.17	0.13
Specific surface area (cm^2/g)	900	1,000	1,500

It is not clear why free sulphuric acid content in liquid gives influence on agglomeration of gypsum. It is supposed that sulphuric acid will effect on equilibrium of aluminium-fluoride complex formation or involvement of such complex in gypsum crystal. As can be seen in Table III, gypsum is less agglomerated when sulphuric acid content in liquid is higher.

6. CONTROL OF CRYSTAL TYPE

When gypsum is used for gypsum board production, sometimes it is required to control the gypsum quality between agglomerated and single crystal in order to keep a certain short setting time and product strength at the same time and the control is possible by changing sulphuric acid content or fluorine content in hydration liquid.

Sulphuric acid content in hydration liquid can be changed easily and independently to fairly a large extent (0 - 10 %) and by this method crystal nature can be controlled to some extent but not sufficiently only by this method.

It is difficult to control aluminium content in liquid but fluorine ion content can be changed by adding active silica to either digester or hydration tank. By addition of silica, fluorine ion is converted to fluorosilicic ion. Fluorosilicic acid is evolved easily and even for the remaining fluorine in liquid it does not form complex material with aluminium and hinders involvement of aluminium-fluorine complex in gypsum because it is fluorosilicic ion and not fluorine ion.

Table IV. Influence of Silica Addition

Silica added (kg/t P_2O_5)				
to Digester	0	20	40	0
to Hydration tank	0	0	0	40
Al_2O_3 in liquid (%)	0.9	0.8	0.7	1.2
F^- in liquid (%)	1.3	0.9	0.5	0.2
Al_2O_3 in gypsum (%)	0.4	0.2	0.1	0.1
Specific surface area (cm^2/g)	900	1,000	1,100	1,200

Table IV shows the example of influence of silica addition on gypsum crystal. It is clearly seen that the addition of silica either to digester or hydration tank is effective in decreasing aggromeration and addition to hydration tank is more effective.

7. QUALITY IMPROVEMENT FOR H_2SO_4/CEMENT PROCESS

As mentioned in Section 3.4, it is required to reduce total fluorine content in gypsum when it is used for cement and sulphuric acid process. Most fluorine in gypsum is in the form of sodium fluorosilicate and it can be removed by water washing. But when fluorine exists in water insoluble form, such as calcium fluoride, chukhrovite, etc., it is difficult to remove from gypsum and measures must be taken to make water insoluble fluorine in gypsum less.

Here again by adding silica to either digestion section or hydration section, existence of fluorine ion in liquid is reduced and formation and involvement of water insoluble fluorine compound into gypsum is depressed.

CONCLUSION

When using gypsum from hemi-dihydrate strong acid phosphoric acid process, in which gypsum crystal has tendency to aggromerate due to accumulation of aluminium in hydration liquid, it is sometimes required to reduce the degree of aggromeration in order to shorten the setting time of calcined gypsum in the process of gypsum board production.

It was found that the addition of active silica to reaction sections reduces the degree of aggromeration and shorten the setting time. By this method, we are controlling the quality of gypsum from our phosphoric acid plant to meet the requirements of gypsum board plant, though the theoretical analysis of the phenomena is not yet sufficient.

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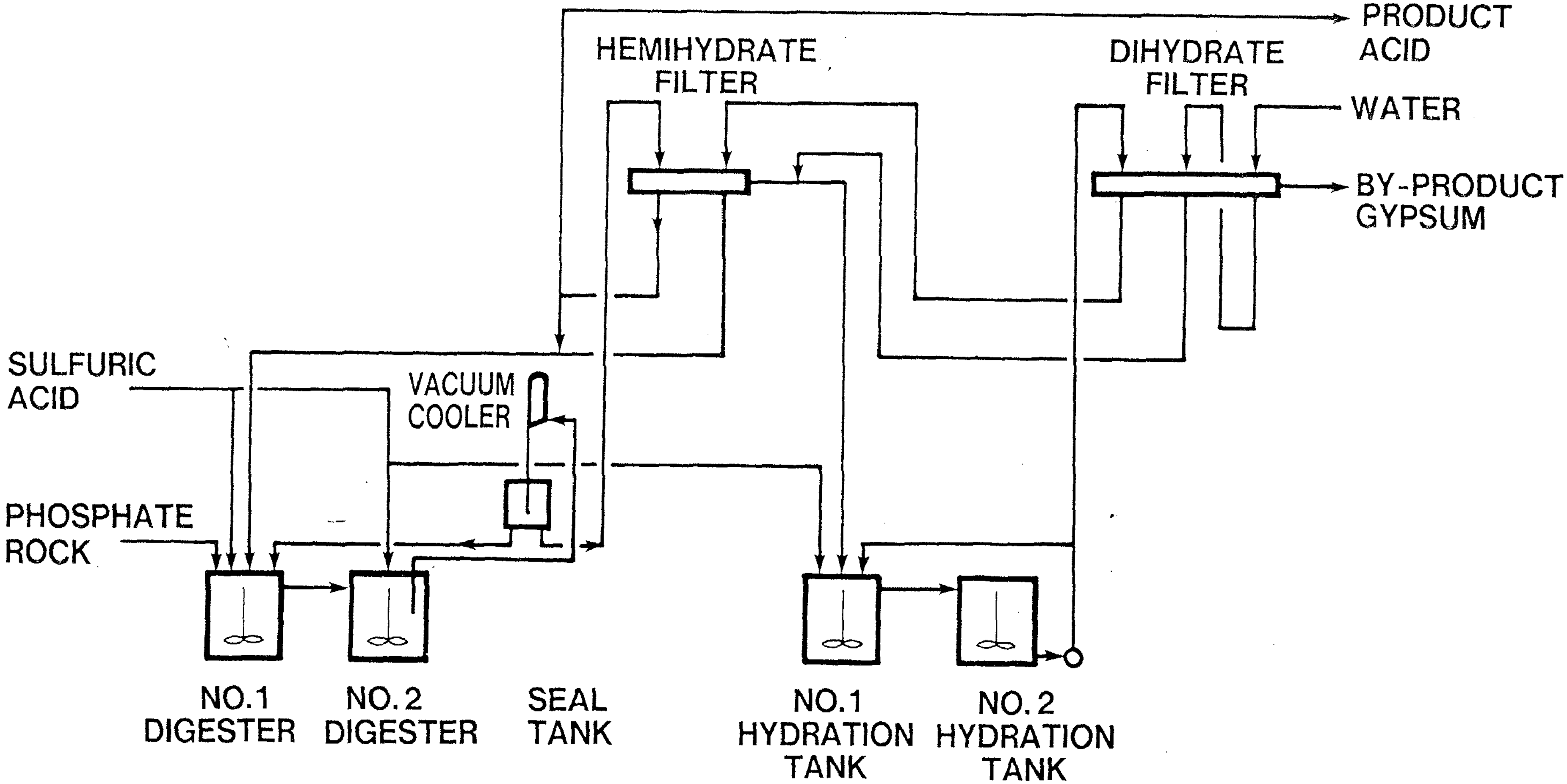
SCHEMATIC FLOW DIAGRAM OF NISSAN C-PROCEES



NEW PHOSPHOGYPSUM BUILDING MATERIALS BY USING EXTRUSION TECHNOLOGY

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One of the main trends in the chemical industry for processing of the disposed phosphogypsum (PHG) is it's utilization for the needs of the building industry. It is known [1] the production of gypsum ware from natural and chemical gypsum by pressing and moulding is accompanied by considerable technological difficulties such as: the impossibility of producing large size elements; the low productivity; the limitations in shape and configuration; the deformation and the low physico-mechanical indices of the ware. The newly developed extrusional method for PHG processing to building materials [2-4] permits to overcome these shortcomings.

The application of the extrusional method for moulding of PHG ware imposed the solution of two main problems connected with the preparation of PHG-β hemihydrate, enabling the regulation of its bonding time and with the hydro-modifying of the extrusional bulk brior to its moulding.

The known retardents of the process of natural gypsum hydration have no effect on the beginning and on the rate of hydration of the semihydrate produced without preliminary washing of the PHG or have an insignificant influence. As a result of the investigations carried out a direct method for the preparation of PHG-β hemihydrate from unpurified PHG was developed, permitting to regulate the process of hydration. Practically it includes the introduction to PHG of neutralizing additives of 0,5 to 10% ($CaCO_3$, CaO, $Ca(OH)_2$, phospholime, dolomite, TPS ash etc.) by one of the following methods: by addition to the initial raw PHG with a subsequent dehydration; by addition to the β-hemihydrate of the unpurified initial PHG; by addition to the water required for the extrusional process. The studies were carried out with PHG produced by processing of "Kolla"-apatite with the following composition $P_20_{5t.}$ - 1,4%, $P_20_{5\ w.s}$. - 0,9% and F - 0,4%.

The experiments over the PHG β-hemihydrate preparation revealed that it is possible to produce β-hemihydrate suitable for the production of building ware by the extrusional method if the dehydration being carried out at 125-145°C without suction of the steam separated and at l15-125°C with purging of the steam. An intermediate is obtained under the above mentioned conditions with the following composition: $CaSO_4$.0,5%, H_2O - 93,5%, $CaSO_4$-III - 1%, $CaSO_4$-II - 5% and $CaS0_4.2H_20$ - 0.5%.

The wide range studies on the acidity of PHG and its mixtures with neutralizing additives revealed that the deterioration of the bonding properties of the β-hemihydrate is caused mainly by the $CaSO_4$-II whose formation is accelerated by acidic phosphoric and fluoride compounds in the absence of neutralizing additives.

A kinetic study was carried out on the kinetics of the PHG-β-hemihydrate hydration related to the quantity (0,1-2%) and the type of the retardent applied: penrog, bone glue lime, citric acid, boric acid, acetates, oxalates, citrates, phosphates, etc.) The penrog was selected for further investigations and for practical application. It is possible to introduce it to the semihydrate in a water solution or directly with the water required for the hydration process.

The data on the initiation time (τ_e) produced from preliminary washed PHG or from $CaCO_3$ neutralized PHG are almost identical. This confirms the advantages of the method developed for the direct-semihydrate preparation without preliminary washing and additional processing of PHG. By applying the above mentioned retardents this method enables the regulation and the increase of hydration time τ_i and τ_e in accordance with the requirements of the technology for extrusional PHG were production.

It was also studied the hydration kinetics of the β-hemihydrate produced in the presence of neutralizing additives and retardents and it was established that it is fitted by the equation of Ridge [5]:

$$\frac{d\alpha}{d\tau} = k\alpha(1-\alpha)^{2/3},$$

where α is the degree of hydration, k is a constant and τ is time.

The kinetic parameters of the process were determined and a mathematical model describing the effect of the neutralizing additive (x_1,%), the retardent - penrog (x_2,%), the total quantity of moisture (x_3,%) and the temperature (x_4,^{0}C) on the constant in the equation of Ridge was derived:

$$K = -0.0012-0,1193X_1+0,1739X_2+0,0041X_3+0,0034X_4+0,0016X_1^2$$
$$+0,1404X_2^2-0,0003X_3^2-0,00002X_4^2-1,3313X_{1,2}+0,0069X_{1,3}$$
$$-0,00017X_{1,4}+0,0695X_{2,3}-0,0031X_{2,4}-0,00004X_{3,4}.$$

The data analysis and the regresional equation obtained revealed that, the content of the neutralizing additive ($CaCO_3$) and that of the retardent in the PHG-B-hemihydrate mixture, exerted greatest influence on K. When they increase, the Ridge's equation constant decreases, as it is more sensitive for $CaCO_3$ contents in the mixture up to 2%. As distinguished from the process of the hydratation of the PHG-β-hemihydrate solely, the temperature effect on the constant K is insignificant in the presence of a neutralizing additive and a retardent. All these facts confirm the complex character of the retardent on the kinetics of the hydratation process of β-hemihydrate, directly prepared by dehydrating the initial commercial PHG - dihydrate. It is inexpedient for practical aims, to increase the quantity of the neutralizing additive ($CaCO_3$) above 2%, due to the resulting decrease of the strength parameters of ware, so that this quantity may be considered as optimal. In this case the regressional equation of the dependence of K is simplified to:

$$K = -0,2335-2,4888X_2+0,0179X_3+0,0031X_4+0,1404X_2^2-0,0003X_2^2-$$
$$-0,00002X_4^2+0,0695X_{2,3}-0,0031X_{2,4}-0,0000X_{3,4}.$$

After substituting the expression obtained in the equation of Ridge, a modified kinetic equation results, which fitted very well the experimental data:

$$\frac{d\alpha}{d\tau} = \begin{bmatrix} -0,2335-2,4888X_2+0,0179X_3+0,0031X_4+0,1404X_2^2 \\ -0,0003X_3-0,00002X_4^2+0,0695X_{2,3}-0,0031X_{2,4}- \\ -0,00004X_{3,4} \end{bmatrix} \alpha(1-\alpha)^{2/3}$$

This equation permits to determine the conditions of the PGH-β-hemihydrate, hydratation and to control the process of preparation of extrusionally moulded ware. The time of initiation of the hydration (τ_i) is equal to 2-4 h for mixture containing: $CaCO_3$ 2%, penrog up to 0,4%, total moisture 33-35%, completely up to the requirements for a constant rheology of the mixture and for carrying out the extrusion.

The laboratory experimental data were tested on a semi-industrial installation for the dehydratation of PHG a capacity of 1 ton of β-hemihydrate per hour. It consisted of a vertical dryer (d = 0,5 m and h = 18 m) where the free moisture in the initial PHG was separated and a horizontal dryer (d = 0,325 m and 1 = 3,0 m) with indirect heating and cooling of PHG where $CaSO_4.2H_2O$ is converted into hemihydrate with the following composition: $CaSO_4.0,5H_2O$ - 85%, $CaSO_4.2H_2O$ - 7%, $CaSO_4$-III - 0,3%, $CaSO_4$-II - 7%, H_2O - 6,6%.

This PHG was used to investigate the effect of the initial composition on the rheological properties of the extrusional bulk and on the physico-mechanical indices of the PHG ware produced. The extrusional mixture consisted of: β-hemihydrate, fillers ($CaCO_3$, $Ca(OH)_2$, CaO, phospholime, cement, pyrite dross, TPS ash, etc.) hydromodifiers (Polyox, Methocel, carboxymethyl cellulose, hydroxypropylcellulose, lignin sulphonates, etc.) hydration regulators (penrog, bone glue, Retardent-P, etc.), reinforcing additives (asbestos, glasswol, mineral wool, paper, chemical fibers, etc.), hydrofobizating agents, dyes, etc. IT's effect on the rheological properties of the bulk was evaluated by the extrusional resistance and by the strength of the extension measured by a rheometer "Netsch 405". The physico-mechanical indices such as volume weight, pressure strength and bending strength were determined by the standard techniques for samples produced by a laboratory vaccum extruder-press "Netsch" after a period of 7 days staying for the conclusive ending of the hydration, process.

On the ground of the experimental data theoretical conclusions were made and the optimal compositions and conditions for the production of the extrudated PHG-ware were selected. A model composition includes (%): 70 PHG - hemihydrate; 1,4 $CaCO_3$; 3,5-asbestos; 0,3 - Badimol; 0,8-penrog; 24 - H_2O. These results were confirmed by the data from experiments carried out in semi-industrial and industrial conditions where prefabricated band elements or panels were produced with the following dimensions: 100-600 mm wide, 15-120 mm thick and up to 6000 mm long, with an emptyness up to 60%.

They are characterized by the following indices: pressure strength over 105 kg/cm^2, bending strength over 75 kg/cm^2, volume weight 1,55-1,65 kg/cm^3 and possess good sound and thermal isolating properties.

The application of the extrusional method for the production of PHG ware enables to extent the range of the building ware produced. The application of a continuous technology on an installation with high capacity and quality indices of the ware permitting the mechanization and the automation of the production process.

The newly developed technology (Fig. 1) for the production of the extrudated PHG ware presents a new and rather perspective trend for the utilization of PHG supplying new types of building materials. The technological process includes three main stages: 1) fixing and mixing the initial components; 2) extrusion, cuting and calubrating of ware; 3) hydration of the moulded ware.

REFERENCES

1. Y.I. Richter, Proizvodstvo Gypsovych Vyazustych Veshtestv, Moscow, Vysshaya Shkola, 1974.
2. Bulg. Pat. No 29907; 7.05.1975.
3. Bulg. Pat. No 33463; 14.06.1976.
4. Bulg. Pat. No 57310; 7.10.1986.
5. M.J. Ridge, Nature, 204, No 3, 70-71, 1964.

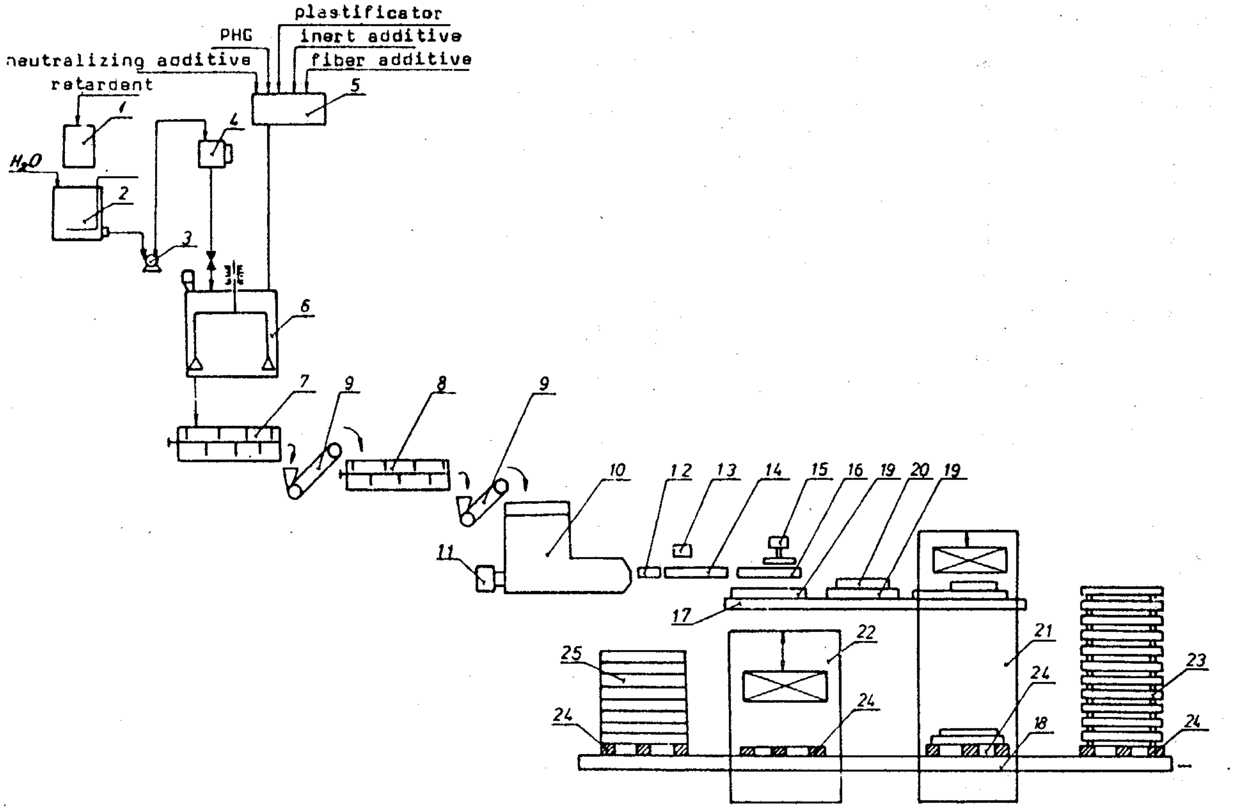

Fig. 1. Principal technological scheme of the preparation of extrudated phosphogypsum panels: 1,2 - tanks; 3 - pump; 4 - sight; 5 - weights; 6,7,8 - mixers; 9 - belt conveyor; 10 - extruder-press; 11 - electric drive; 12,14,16,17,18 - roller bearing; 13 - cutting device; 15 - calibrating device; 19 - saddle; 20 - panel; 21,22 - manipulators; 23 - panels for hydratation; 24 - pallet;