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PROCEEDINGS OF THE THIRD INTERNATIONAL SYMPOSIUM ON PHOSPHOGYPSUM

VOLUME I

GREAT SEAL OF THE STATE OF FLORIDA
IN GOD WE TRUST

Organized by
The University of Miami
under a grant sponsored by the
Florida Institute of Phosphate Research
Bartow, Florida

December 1990

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 by telephone.

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DISCLAIMER

TABLE OF CONTENTS

Volume I

SOIL AMENDMENT

Volume II

UTILIZATION

CONSTRUCTION

POTENTIAL ENVIRONMENTAL HAZARDS OF PHOSPHOGYPSUM STORAGE IN CENTRAL FLORIDA

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The views expressed in this paper are the author's and do not necessarily reflect official US EPA policy.

ABSTRACT

Phosphogypsum is the primary byproduct generated from phosphoric acid production. A slurry of phosphogypsum is pumped to onsite disposal areas termed phosphogypsum stacks. Phosphogypsum settles out of the slurry and acidic process water is recycled. Rainwater and remaining process water combine to form a hydraulic head, forcing the infiltration of acidic stack water (leachate) into aquifer systems. Phosphogypsum is primarily hydrated calcium sulfate (approximately 96%), but it is contaminated with naturally occurring metals and radionuclides. Recycling process water concentrates these contaminants in the phosphogypsum. Contaminants of concern include As, Cd, Cr, Pb, Na, F, Mn, U-238 and U-234 and uranium decay products. Contaminants emanating from phosphogypsum stacks impact the environment and nearby human residents. Sources of contamination include: stack water leaching into aquifers and surface water systems; the gaseous diffusion of Ra-222 into air; airborne suspension of radionuclide bearing particulate matter; and direct irradiation from gamma radiation. Human health risk assessments associated with environmental contamination from stacks indicate that the potential risks decrease as a function of distance from the stack. Appropriate mitigation techniques, such as dust control, crust formation, a large buffer zone, and leachate collection and lining requirements for new or expanded stacks reduce potential human health impacts. A Federal Rule (NESHAPS, 1989) and a Florida Policy Statement (Nov. 9, 1989) were developed to reduce environmental contamination associated with stacks. The NESHAPS Rule requires average radon emissions to be below 20 pCi/m^2set and requires that phosphogypsum be stored in stacks.

HISTORICAL PERSPECTIVE

Region IV Environmental Protection Agency (EPA) issued in 1978 the Final Areawide Environmental Impact Statement (Areawide EIS) on the Central Florida Phosphate Industry. This EIS was generic in nature because it addressed National Environmental Policy Act (NEPA) compliance procedures for the issuance of new source National Pollutant Discharge Elimination Standards (NPDES) permits specific to central Florida phosphate mining. The Areawide EIS addressed atmospheric, surface water, land use, and radiation issues, but it did not focus on impacts of phosphogypsum on the environment.

Since the original Areawide EIS was issued, new environmental data are available that provide technical information on groundwater impacts and radionuclide emissions from phosphogypsum. In 1986

Region IV participated in a groundwater monitoring program in cooperation with EPA Cincinatti's Office of Research and Development (ORD) and the Florida Institute for Phosphate Research (FIPR). The results were summarized in the report "Phosphate Chemical Processing Facilities Groundwater Chapters" (Bromwell and Carrier, 1987). In addition, Region IV EPA conducted radionuclide emission monitoring in cooperation with EPA's Office of Radiation Programs in Washington, D.C., and Eastern Environmental Radiation Facility (EERF) in Montgomery, Alabama. The results were summarized in the EPA document "A Long-Term Study of Radon and Airborne Particulates at Phosphogypsum Stacks in Central Florida" and published in 1988 (Horton et al., 1988). During this same time period, EPA's Office of Radiation Programs (ORP) was charged with determining whether or not radionuclide standards should be issued for phosphogypsum stacks under the Clean Air Act and EPA's Office of Solid Waste (OSW) was charged to recommend to Congress whether or not the stacks of waste phosphogypsum should be regulated under the Resource Conservation and Recovery Act (RCRA). EPA's ORP National Emission Standards for Hazardous Air Pollutants (NESHAPS, 1989) requires that all phosphogypsum be stored in phosphogypsum stacks and that radon emissions be below 20 pCi/m^2 -sec. EPA currently requires that phosphogypsum be disposed in stacks or mines, which precludes alternative uses of the material, except for a limited class waiver for the agricultural use of phosphogypsum, which will be in effect until October 1, 1990 (FR 1989 51654). EPA has, however, announced a limited reconsideration of the rule requiring the disposal of phosphogypsum in stacks or mines, and has also given notice of a "proposed rulemaking by which EPA is proposing to maintain or modify the rule to, alternatively or in combination, (1) make no change to 40 CFR Part 61, Subpart R, as promulgated on October 31, 1989, (2) establish a threshold level of radium-226 which would further define the term "phosphogypsum," (3) allow, with prior EPA approval, the use of discrete quantities of phosphogypsum for researching and developing processes to remove radium-226 from phosphogypsum to the extent such use is at least as protective of public health as is disposal of phosphogypsum in mines or stacks, or (4) allow, with prior EPA approval, other alternative use of phosphogypsum to the extent such use is at least as protective of public health as is disposal of phosphogypsum in mines. EPA's OSW recommended to Congress that phosphogypsum be retained under the Beville Mining Waste exclusion (40 CFR Part 261, EPA/OSW-FR-89-025) and not be regulated as a hazardous material under the Resource Conservation and Recovery Act (RCRA). In addition, the State of Florida, issued a Policy Memo on November 29, 1989 which states that phosphogypsum is a solid waste under Florida Statutes (F.S.) Section 403.703(13) and is also classified as a special waste within F.S. 403.703(34).

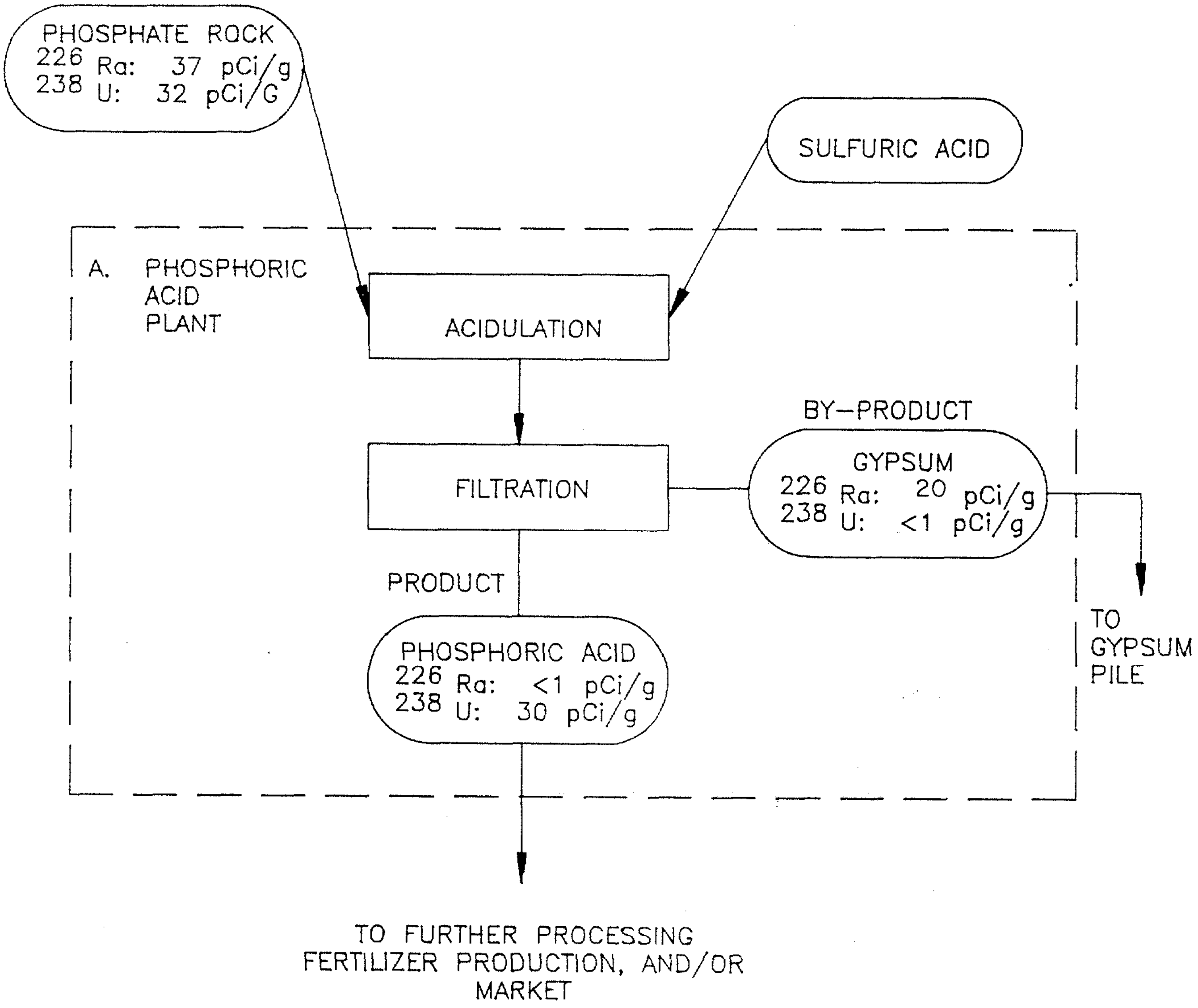
PHOSPHATE PRODUCTION SUMMARY

The Central Florida Phosphate District encompasses phosphate ore deposits underlying an area of approximately 5180 square kilometers (2000 square miles) in Polk, Hillsborough, Manatee, Hardee, Sarasota, and DeSoto Counties (Cathcart, 1971). For the purposes of this study, additional deep phosphate ore deposits in Charlotte County are also included. In the years since 1975, annual phosphate ore production peaked at approximately 43.0 million metric tons and is currently (1987) about 30.0 million metric (33.0 million short) tons. This current rate of production supplies approximately eighty percent of the U.S. phosphate demand (Florida Phosphate Council, 1988). In the United States phosphate rock is primarily used in the production of commercial fertilizer.

Phosphate ore from the beneficiation plant is treated with sulfuric acid and water to form phosphoric acid and the solid by-product, phosphogypsum (Figure 1). The phosphogypsum slurry is pumped to a phosphogypsum stack where evaporation and leaching of the free water occurs. Most process water is decanted and recycled. The retained pore water forms an impeded pressure head within a phosphogypsum stack which acts as a driving force for the leaching of water vertically and/or laterally into the underdrains or underlying aquifer. After evaporation and water recovery, large piles remain, typically three to sixty meters high and covering as much as 200 hectares (494 acres). For each ton of phosphoric acid produced about five metric tons of phosphogypsum are formed as a solid by-product. It is estimated that by the year 2000, approximately 900,000,000 metric tons of phosphogypsum will be present in Florida in phosphogypsum stacks (May and Sweeney, 1982).

WASTE DISPOSAL

Waste products generated by the phosphate industry include the clay slime and sand resulting from the ore extraction/beneficiation process, Wastewater effluents, air emissions, and phosphogypsum from the chemical plants. The Florida Department of Environmental Regulation (DER) has identified 20 phosphogypsum stack systems of which 17 are located in Polk, Hillsborough, and Manatee Counties. A phosphogypsum stack system is defined by DER as the phosphogypsum and associated process water, cooling ponds, and conveyance ditches. Fifteen of the 20 systems are active and receive phosphogypsum along with recirculated process water each day the facility operates. The process water is acidic, containing sulfuric and phosphoric acids from the reaction of sulfuric acid with phosphate ore to produce phosphoric acid. In the process of reacting phosphate matrix with sulfuric acid, a number of materials are solubilized into the liquid phase. The materials include arsenic, cadmium, chromium, lead, sodium, fluorides, manganese, iron, sulfates, and radionuclides. Some facilities are operated as essentially zero-discharge to surface

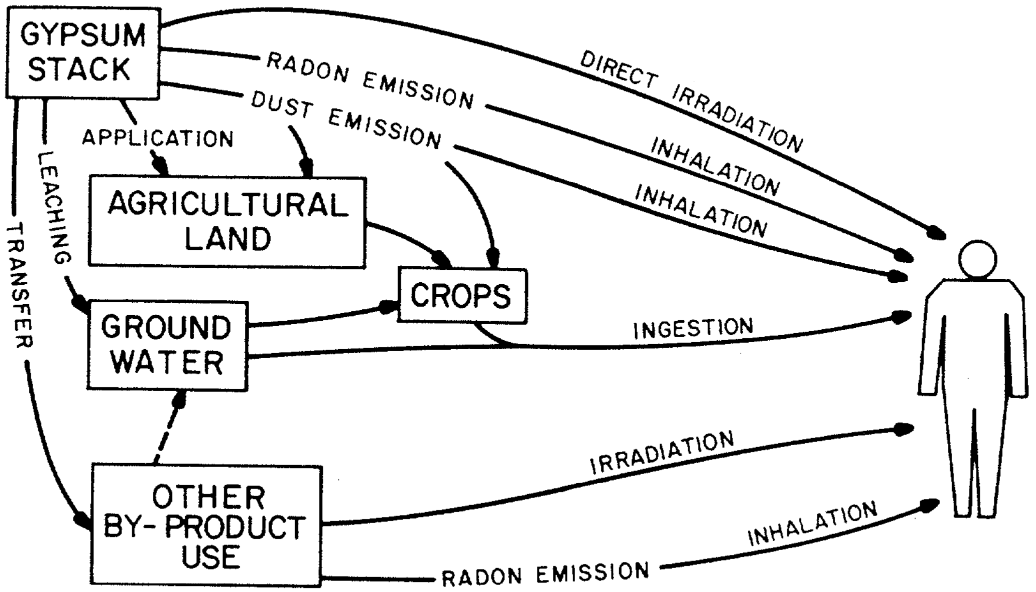


NOTE: RADIONUCLIDE CONCENTRATIONS
ARE FOR CENTRAL FLORIDA.

SOURCE: ROESSLER ET., 1979

SIMPLIFIED FLOW CHART
FOR WET PROCESS
PHOSPHORIC ACID PRODUCTION

FIGURE 1



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SOURCE: ROESSLER, 1987

POTENTIAL RADIONUCLIDE PATHWAYS TO HUMANS

FIGURE 2

waters. A chemical plant process-water cooling canal is generally located at the base of the stack slope and extends around the entire perimeter of the stack. Process water from the chemical plant is circulated through this canal and returned to the plant for reuse. The canal also intercepts some of the leachate from phosphogypsum stack dewatering. If the stack has a synthetic or natural liner, the dewatering is primarily by evaporation and by leachate collection in the cooling canal. For most currently operating stacks, leachate percolates downward and laterally though the soils and groundwater. Some stack water can be recaptured by drain systems. Depending on the local geology and other relevant factors, leachate percolation is usually a source of groundwater contamination.

POTENTIAL EXPOSURE PATHWAYS

Contaminants emanating from phosphogypsum stacks potentially impact the environment and human populations. Potential pathways of exposure to humans include: direct irradiation from gamma radiation; airborne emissions of radon and dust (radioactive and non-radioactive) and other carcinogens; and ingestion of contaminated groundwater. Figure 2 graphically summarizes these and other potential pathways.

PHOSPHOGYPSUM AND CONTAMINANTS

Phosphogypsum is primarily hydrated calcium sulfate (about 96%): contaminants include acidic process water, water soluble fluoride, radionuclides and numerous heavy metals. Phosphogypsum typically contains appreciable quantities of uranium and its decay products. This is due to the high uranium concentration in phosphate rock which ranges from 6.7 to 67 pCi/g uranium (U-238) and averages about 40 pCi/g (Roessler et al., 1979; Lardinoye and Weterings, 1982). This is about 10 to 100 times U-238 amounts in other Florida geologic substrates. Radionuclides of concern are: U-238, U-234, thorium (Th-230), radium-226 (Ra-226), radon-222 (Rn-222), lead-210 (Pb-210), and polonium-210 (Po-210). Many of these contaminants survive the mining, beneficiation, and chemical processing and accumulate along with phosphogypsum.

During the wet processing of phosphate rock, there is selective separation and concentration of radionuclides (Figure 1). Uranium is separated from radium and associates with phosphoric acid, while radium associates primarily with the phosphogypsum. The activities of U-238 and Ra-226 in the phosphoric acid are typically about 30 and less than one pCi/g, respectively. In the phosphogypsum, the radium and uranium activities are typically on the order of 20 and less than one pCi/g, respectively.

Average radionuclide concentrations of uncontaminated Central Florida soils and of phosphogypsum are presented in Table 2-1. The radionuclide concentrations in phosphogypsum exceeded those in background soils by 10 times for U-234 to 60 times for Ra-226. The radionuclide concentrations were similar to previously reported data (Roessler, 1987).

pCi/l	WL	Estimated number of lung cancer deaths due to radon exposure (out of 1000)	Comparable exposure levels		Comparable risk
200	1	440 - 770	100 times average outdoor level		More than 60 times non-smoker risk 4 pack-a-day smoker
100	0.5	270 - 630	100 times average indoor level		20,000 chest x-rays per years
40	0.2	120 - 380			
20	0.1	60 - 210	100 times average outdoor level		2 pack-a-day smoker 1 pack-a-day smoker
10	0.05	30 - 120	10 times average indoor level		5 times non-smoker risk
4	0.02	13 - 50			
2	0.01	7 - 30	10 times average outdoor level		200 chest x-rays per year
1	0.005	3 - 13	Average indoor level		Non-smoker risk of dying from lung cancer
0.2	0.001	1 - 3	Average outdoor level		20 chest x-rays per year

WL = Working Level

Radon Risk Evaluation Chart

Figure 3

Table 2-1. Average radionuclide concentrations in phosphogypsum and background soils. Values are means of samples taken from five stacks (Horton et al., 1988).

Material	Ra-226	U-234	U-238	Th-230	Po-210	Pb-210
			(pCi/g)			
Phosphogypsum	31	3.3	3.2	5.1	27	36
Background soil	0.5	0.3	0.3	0.3	0.5	0.7

Airborne Emissions

The two principal mechanisms for the airborne release of radionuclides from phosphogypsum stacks are: the diffusion of Rn-222 into the air and the suspension of radionuclides particulates from vehicular traffic and wind.

Radon Flux. Radon flux, which is the rate at which radon emanates from the surface of the stack, is a measure of the amount of Rn-222 activity (measured in Curies) that escapes from a given area of stack surface (square-meters) during a given time (second). One picoCurie (pCi) is 1 x 10^{-12} Curies. The amount of radon emanating from phosphogypsum stacks is proportional to many variables, including: the stack area, Ra-226 and Rn-222 concentrations in the phosphogypsum material, emanation fraction, crust depth, vegetation cover, moisture content, activity level and climatic conditions. Emanation rates vary spatially and temporally on each stack and between stacks. Modeling of Rn-222 emission rates is very difficult, costly and requires flux measurements.

Previous research indicates that the best Rn-222 emission estimates are derived from dividing phosphogypsum stacks into source sections, as in Table 2-2. Each source section reflects a characteristic emission rate. For each source, emission rates are high on non-crusted, actively worked surfaces, but are less than one pCi/m^2/s on areas covered by water (ponds and ditches). Detailed Rn-222 flux measurements were presented for phosphogypsum stacks in Florida by Horton et al., (1988) and Blanchard and Horton, (1988). The data indicate a extremely wide variation in Rn-222 flux rates by source section. Characteristically, the highest radon emission rates come from loose-dry material and stack sides.

Table 2-2. Results of radon-222 flux measurements on phosphogypsum stacks in Florida (NESHAPS, 1989).

Stack Region/Facility	Number of Measurements	Flux (pCi/m^2/s) Range	Flux (pCi/m^2/s) Average(a)
	ACTIVE STACKS		
Top			
Loose-Dry Material			
Conserve (Mulberry, FL)	128	2 - 340	25
Gardinier (East Tampa, FL)	336	0.2 - 99	20
Grace (Bartow, FL) (b)	519	0.2 - 65	16
Royster (Mulberry, FL)	126	0.6 - 81	21
Beaches (c)			
IMC Corp. (Mulberry, FL)	6	0.35 - 0.71	0.5
Roadway (dry-hard pack)			
Grace (Bartow, FL) (b)	23	1.2 - 16	7
Sides			
Royster (Mulberry, FL)	98	1.3 - 23	7
Grade (Bartow, FL) (b)	75	1.7 - 40	11
	INACTIVE STACKS		
Top			
Estech (Bartow, FL)	130	0.6 - 14	4
Sides			
Royster (Mulberry, FL)	99	4 - 44	15

(a) Average values are the arithmatic means.
(b) Now the Seminole Fertilizer Corporation
(c) Baretincic, J.M., IMC Fertilizer, Inc. June 1988.

As part of the NESHAPS (1989) report, annual total Rn-222 emission rates per stack were calculated. The estimates were made by multiplying flux rate estimates by representative stack sections and summing. A stack used by IMC, near Mulberry, Florida was used as a model stack to estimate various stack source sections. Additional assumptions and details are provided in the NESHAPS (1989) report. Estimates of the annual Rn-222 emissions from individual phosphogypsum stacks are presented in Table 2-3. Total Rn-222 emissions in Florida are estimated at approximately 3000 Ci/yr, which is about one-half of the total Rn-222 released across the nation from all phosphogypsum stacks (NESHAPS, 1989).

Table 2-3. Estimates of radon-222 emissions from phosphogypsum stacks in Florida (NESHAPS, 1989).

Facility Name	Location	Rn-222 Emissions (Curies)	Average Rn-222 Flux ($pCi/m^2/s$)
Agrico Chemical Co.	Bartow, FL	250	5.7
Royster Phosphate, Inc.	Palmetto, FL	220	5.7
Brewster Phosphates	Bradley, FL	92	5.8
CF Industries, Inc.	Plant City, FL	310	6.0
CF Industries, Inc.	Bartow, FL	340	7.2
Conserv. Inc.	Nichols, FL #1	58	5.7
	#2	71	7.0
Estech, Inc.	Bartow, FL	27	7.7
Farmland Ind., Inc.	Bartow, FL	170	5.8
Gardinier, Inc.	Tampa, FL	310	6.9
Seminole Fert. Corp.	Bartow, FL	100	4.9
Seminole Fert. Corp	Bartow, FL	400	5.6
IMC Corp.	Mulberry, FL	290	5.7
Occidental Chemical CO.	W. Springs, FL #1	36	2.8
(Suwannee River)	#2	35	2.7
Occidental Chemical Co. (Swift Creek)	White Springs, FL	43	2.5
Royster Co.	Mulberry, FL #1	62	6.4
	#2	43	7.3
USS Agri-Chemicals, Inc	Bartow, FL	59	9.1
USS Agri-Chemicals, Inc.	Ft. Meade, FL	120	6.1

Airborne radon concentrations. Horton et al. (1988) reported airborne radon-222 concentrations above and around a phosphogypsum stack for the purpose of determining if an increase in airborne radon concentration was detectable above background levels. Radon-222 concentrations in air were obtained one meter above the ground next to five phosphogypsum stacks using alpha-track detectors. Background concentrations were measured at nine locations that were at least eight kilometers (five miles) from any phosphogypsum stack. Measurements were made continuously during the study using three, four-month exposure periods. Because of the continuous operations being conducted on the active stacks by plant personnel, it was not possible to place the detectors on the top surface of the stacks. Rather, the detectors were placed around the perimeter at the base of the stacks with a larger number in a predominantly downwind direction.

The average radon-222 concentrations measured at the base of five phosphogypsum stacks (average over four active stacks) was 0.66 pCi/l and exceeded the background concentration (0.13 pCi/l) by five times. Roessler (1985) studied an existing phosphogypsum stack for radionuclide content, radon emissions, and airborne radon concentrations. Ra-226 in phosphogypsum was 24.3 pCi/g, with values ranging from 21 to 28 pCi/g. Radon flux averaged 23 pCi/m^2-sec. Airborne radon values varied from 0.3 to 0.4 pCi/l on and near the stack, with concentrations decreasing to background levels (0.13 pCi/l) at a distance of about 1000 meters.

Airborne particulates. Airborne particulates are primarily emitted from phosphogypsum stacks as a result of wind erosion or vehicular traffic on the stacks. Because phosphogypsum contains naturally occurring radionuclides, the emitted particulates may represent a source of exposure to radiation. Wind suspended particulate emissions are not a significant source of radioactivity because of the moisture content of the phosphogypsum in operating stacks and the crust that forms on inactive stacks. Emission rates due to vehicular traffic only were estimated as part of the NESHAPS (1989) report. Total annual radionuclide emissions were estimated by multiplying the total annual estimated emissions (19.7 million g/yr), by the average concentrations of radionuclides in phosphogypsum (Table 2-1). Radioactive contamination of the local area is low from particulate material (Table 2-4).

Table 2-4. Annual radionuclide emissions in fugitive dust from a model 31 hectare phosphogypsum stack (NESHAPS, 1989).

Radionuclide	Emission Rate (Ci/yr)	Radionuclide	Emission Rate (Ci/yr)
U-238	6.3E-5	Pb-214(a)	6.1E-4
U-234	6.5E-5	Bi-214(a)	6.1E-4
Th-230	1.0E-4	Pb-210	7.1E-4
Ra-226	6.1E-4	Po-210	5.3E-4
Ra-222(a)	6.1E-4		

Note: Ra-222 is assumed to be in equilibrium with Ra-226 and Pb-214 is assumed to be in equilibrium with Bi-214.

Gamma radiation exposure rates. As a result of the naturally occurring radionuclides in the phosphogypsum, the stacks are a direct source of gamma radiation. Exposure rate from phosphogypsum is a function of many variables, but primarily distance from the stack, the size of the stack and the concentration of gamma-emitting radionuclides in the stack.

In an EPA study (Horton et al., 1988), gamma radiation exposure rate measurements were obtained one meter above the ground surface at several locations on five phosphogypsum stacks. The exposure rates over the stacks were constant, varying by no more than a factor of two, and did not vary significantly between stacks. The average stack exposure rate (mean of four active and one inactive) of 33 microrads per hour exceeded the background exposure rate of five microrads per hour by about six times. Background exposure measurements were made in a region of Polk County, Florida, outside the influence of the phosphate industry.

AIRBORNE HEALTH ASSESSMENT

This section is derived primarily from the NESHAPS (1989) report and assesses the health impacts of airborne emissions from phosphogypsum stacks. Impacts due to radon-222 are estimated based on actual emissions of radon from phosphogypsum stacks in central Florida. Impacts due to particulates are estimated based on models. Impacts for both types of emissions are estimated for the maximum exposed individual and for the population within an 80 kilometer (km) radius of the stack. Gamma radiation impacts were assessed previously EPA (Horton et al., 1988).

Radon. The location of the maximum exposed individual was determined at each stack by using official county highway and U.S. Geological Survey maps to locate the residence nearest to the stack in each of 16 annular sectors. The AIRDOS-EPA and DARTAB codes were then used to estimate the maximum exposure to radon-222 and the highest increased chance of lung cancer for an individual in one of these actual residences (NESHAPS, 1989). The AIRDOS-EPA and DARTAB codes have been combined and are available in the CAP-88 (Clean Air Act Assessment Package-1988) program, as referenced in 40 CFR 61.93(a). Copies of CAP-88 are available from the Radiation Shielding Information Center, Oak Ridge National Laboratory, as package #CCC542.

Collective risks for the regional population due to Ra-222 were calculated from the annual collective exposure (person Working Level Month or WLM) using the computer codes mentioned above. Exposure pathways were identical to those applied to the maximum exposed individual. The population distribution within 80 km of each stack was determined using the computer program SECPOP. Collective exposures to Ra-222 were estimated for each stack by multiplying the estimated Ra-222 progeny concentration (WL) in each annular sector by the population in that sector and by the conversion factor 51.56 WLM/yr per WL. Meteorological parameters from selected nearby weather stations were used for each stack. The cumulative WL exposure of each population segment was adjusted using a radon decay product equilibrium fraction that is related to the distance from the center of the stack to that population segment. An emission height of 1 meter was assumed for all stacks. This is a conservative assumption which may overestimate the maximum individual risk but not significantly in most cases (NESHAPS, 1989).

Table 2-5 lists the highest individual risks for each of the Florida stacks considered in this assessment. Included for each stack is the location of the nearest individual to the stack and the radon-222 concentration and WL exposure at that location. The highest lifetime individual risks are on the order of <1 fatal lung cancers in 10,000.

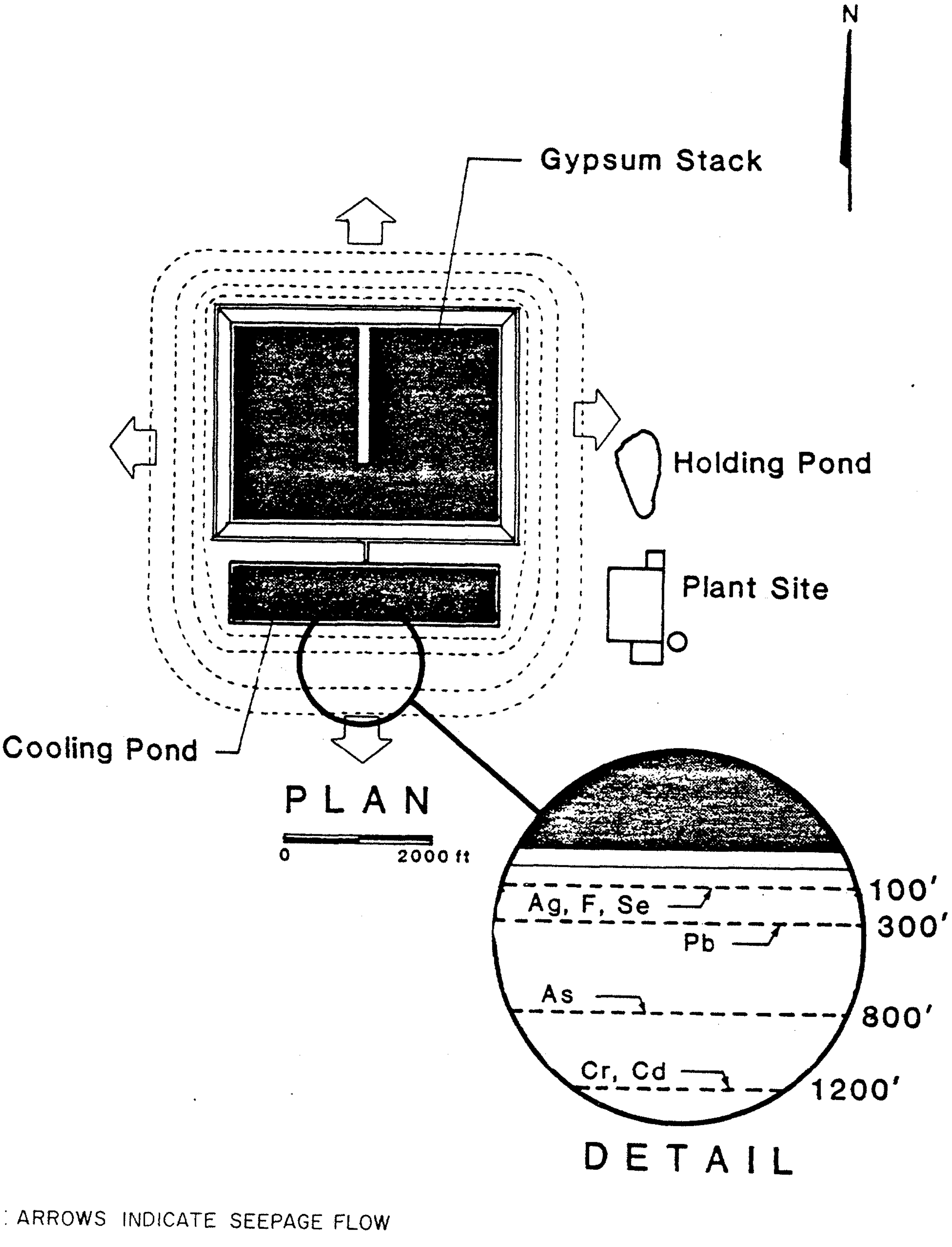
Table 2-5. Estimated lifetime fatal cancer risks to nearby individuals caused by radon-222 emissions from phosphogypsum stacks (NESHAPS, 1989).

Facility/Location	Radon Concentration (pCi/L)	Max. Exposure (WL)	Max. Lifetime Fatal Cancer Risk To Individual	Distance (m)
Agrico Chem. Co Bartow, FL	1.6E-3	7.2E-6	1E-5	4,800
Royster Phos. Inc Palmetto FL	1.8E-2	5.7E-5	8E-5	1,200
Brewster Phos. Bradley, FL	6.8E-3	2.2E-5	3E-5	1,200
C.F. Ind., Plant City, FL	1.5E-2	4.7E-5	6E-5	2,600
C.F. Inc., Bartow, FL	4.2E-3	1.5E-5	2E-5	2,600
Conserv. Inc., Nichols, FL #1	2.3E-3	7.4E-6	1E-5	1,100
#2	2.9E-3	9.1E-6	1E-5	1,100
Estech, Inc. Bartow, FL	5.8E-4	2.2E-6	3E-6	3,000
Farmland Ind., Bartow, FL	8.4E-3	2.8E-5	4E-5	1,500
Gardinier, Inc Tampa, FL	7.7E-3	2.6E-5	4E-5	1,600
Seminole Fert. Bartow, FL #1	8.2E-3	2.6E-5	4E-5	1,200
#2	1.6E-2	5.1E-5	7E-5	1,200
IMC Corp, Mulberry, FL	4.1E-3	1.7E-5	2E-5	4,000
Occidental Chem., Co., #1	8.7E-4	3.3E-6	5E-6	2,800
White Springs, FL #2 (Suwanee River)	7.4E-4	2.8E-6	4E-6	3,000
Occidental Chem., White Springs, FL (Swift Creek)	9.2E-4	3.6E-6	5E-6	3,200
Royster Co., Mulberry, FL #1	3.7E-3	1.2E-5	2E-5	1,000
#2	2.5E-3	7.9E-6	1E-5	1,000
USS AgriChem Inc., Bartow, FL	2.9E-3	9.0E-6	1E-5	900
USS AgriChem Inc., Ft Meade,FL	1.2E-2	3.6E-5	5E-5	1,000

NOTES: 1E-5 = 1 X 10^{-5}
Distance (m) = Distance (in meters) from the center of the stack.

The collective risk due to radon-222 emissions to the 80 km regional population around each phosphogypsum stack are listed in Table 2-6. The populations within the 80 km regions are also listed. This table shows that 1 fatal cancer in 20 years is estimated to occur in the regional population of the Gardinier, Inc. stack which includes the greater Tampa, Florida area (NESHAPS, 1989).

Another way to express the risk associated with radon exposure is to compare it with the risk from other activities. The chart in Figure 3 gives an idea of how exposure to various radon levels over a lifetime compares to the risk of developing lung cancer from smoking and from chest x-rays. The chart also compares these levels to the average indoor and outdoor radon concentrations (USEPA, 1986).



NOTE: ARROWS INDICATE SEEPAGE FLOW

140814

SOURCE: BROMWELL AND CARRIER, INC., 1987

PLUME MIGRATION MODEL
PRIMARY DRINKING WATER
STANDARDS

FIGURE 4

Table 2-6. Summary of committed fatal cancers per year within 80 km of phosphogypsum stacks (NESHAPS, 1989).

Facility/Location		1980 Population (within 80 km)	Committed Fatal Cancers per year (within 80 km)
Agrico Chemical Co., Bartow, FL		1,717,059	2E-2
Royster Phosphate, Inc., Palmetto, FL		2,059,168	2E-2
Brewster Phosphates, Bradley, FL		1,809,809	6E-3
C.F. Industries, Inc., Plant City, FL		2,153,710	3E-2
C.F. Industries, Inc., Bartow, FL		1,698,291	3E-2
Conserv, Inc., Nichols, FL		2,162,868	6E-3
Estech, Inc., Bartow, FL		1,585,674	7E-3
Farmland Industries, Inc., Bartow, FL		1,582,493	2E-3
Gardinier, Inc., Tampa, FL		2,189,940	5E-2
Seminole Fert. Corp., Bartow, FL	#1	1,548,237	9E-3
	#2	1,448,342	3E-2
IMC Corp., Mulberry, FL		2,147,892	3E-2
Occidental Chemical Co.,	#1	214,674	8E-4
White Springs, FL (Suwannee River)	#2	217,985	8E-4
Occidental Chemical Co., White Springs, FL (Swift Creek)		228,859	1E-3
Royster Co., Mulberry, FL	#1	1,734,734	6E-3
	#2	1,780,345	4E-3
USS Agri-Chemicals, Inc., Bartow, FL		1,405,177	5E-3
USS Agri-Chemicals, Inc., Ft. Meade, FL		1,416,722	7E-3

NOTE: 1E-5 = 1 X 10^{-5}

Particulates. The dose equivalents resulting from radioactive particulate emissions were estimated by using airborne pathway models for inhalation, ingestion, ground contamination, and immersion, followed by application of the computer codes AIRDOS-EPA and DARTAB. The maximum annual dose equivalents and the increased risk of fatal cancer to nearby individuals from the fugitive dust emissions were estimated based on the total annual emissions from model stacks using the EPA fugitive dust model (Section 13.2.2, Table 13-8 of the NESHAPS 1989 report) and applying the computer codes mentioned above. The model stacks were assumed to be in Polk County, Florida. An average model stack was derived that had the average base area, 90 hectares (ha), of 27 presently operating phosphogypsum stacks. Also, minimum and maximum generic stacks were considered and assigned base areas of 9 ha and 284 ha, respectively, which reflect the smallest and largest existing active stacks (in the United States). Vehicular traffic on a stack, and thus emissions, is assumed proportional to the stack area. Inactive stacks are assumed to have no vehicular traffic. The study did not investigate the cancer risk posed by other toxic constituents via particle inhalation, but the analysis of the chemical composition of phosphogypsum indicates that chromium and arsenic are present in concentrations which may pose a health risk through this pathway. The greatest concern are for those facilities which have nearby residences.

Collective (population) risks for the region due to fugitive dust emissions from vehicular traffic are based on the assessments of small, average, and large phosphogypsum stacks located in Polk County, Florida, which have areas of 9 ha, 90 ha, and 284 ha, respectively. Emissions from the small, average, and large generic stacks were estimated by multiplying the annual radionuclide emissions from a 31 ha stack by the ratio of their areas, 0.29, 2.9, and 9.2, respectively, as vehicular traffic on a stack is assumed proportional to the stack area. These annual emissions were then applied to the AIRDOS-EPA and DARTAB codes to complete the assessment. The population and its distribution within 80 km of the model stacks were taken from an earlier EPA generic study performed in Polk County, Florida (USEPA, 1984). The meteorological parameters used were taken from the Orlando Jet Port Station.

The dose equivalent rates to the maximum exposed individual due to fugitive dust emissions from three model phosphogypsum stacks are listed in Table 2-7. The areas of the three model stacks relate to the areas of the smallest (minimum), average, and largest (maximum) currently active stacks. It was assumed that the maximum exposed individual resided 1,750 meters from the center of each stack.

Table 2-7. Estimated increased risk of fatal cancer and the dose equ. rates from maximum exposure to fugitive dusts for an individual living near phosphogypsum stacks (NESHAPS, 1989).

Facility	Organ	Dose Equivalent Rate, mrem/yr	Maximum Lifetime Risk of Fatal Cancer
Minimum Model Stack	Lung	0.023	8 x 10^{-8}
	Endosteal	0.040	
Average Model Stack	Lung	0.20	7 x 10^{-7}
	Endosteal	0.37	
Maximum Model Stack	Lung	0.57	2 x 10^{-6}

The last column of Table 2-7 lists the lifetime fatal cancer risks to individuals living 1,750 meters from the center of each model stack. These estimated risks are conservative (i.e., overestimated) because the model treats all particles less than 30 micrometer as having an activity median aerodynamic diameter (AMAD) of 1 micrometer. Even so, these risks due to fugitive dust emissions are one or two orders of magnitude smaller than the risks related to radon-222 emissions.

The collective risks to the regional (0-88 km) population from the radioactivity associated with fugitive dust emissions from the three model phosphogypsum stacks are tabulated in Table 2-8. The population, listed in the second column, is assumed to be the same within the three regions. The risk for the average of 27 active stacks is 2×10^{-4}, or about two fatal lung cancers in 10,000 years. In the last line of Table 2-8 is an estimate of the collective risk, due to fugitive dust emissions, to all 27 regional population within 8 km of an active phosphogypsum stack. This risk, 5×10^{-3} (2×10^{-4} x 27 stacks), is a maximum risk because all particles less than 30 micrometer are assumed in the assessment to have an AMAD of 1 micrometer and to be respirable.

Table 2-8. Estimated number of fatal cancers from fugitive dust emissions for the population living within 80 km of the model phosphogypsum stacks (NESHAPS, 1989).

Facility	Population within an 80-km Radius	Collective Risk (Committed Fatal Cancers per Year)
Minimum Model Stack	1,500,000	3×10^{-5}
Average Model Stack	1,500,000	2×10^{-4}
Maximum Model Stack	1,500,000	7×10^{-4}
Total United States ([a])	41,000,000	5×10^{-3}

(a) Collective risk to all individuals living with 80 km of the 27 active phosphogypsum stacks, assuming the same generic population for each stack (i.e., 27 x 1,500,000 = 40,500,000)

Gamma radiation. Gamma radiation emitted by radionuclides near the surface of a gypsum stack diminishes rapidly with distance. While the emitted radiation levels may contribute to the health risk at a nearby residence or possibly an phosphate industry employee, health risks for members of the general public greatly diminishes with distance from the stack. Therefore, the population exposure to irradiation directly from a phosphogypsum stack is effectively limited to those persons working on living directly next to a phosphogypsum stack.

GROUNDWATER

Several inorganic constituents of phosphogypsum which enter groundwater were selected as significant impact assessment parameters based upon the relative concentrations of each constituent. Exceedances of EPA Primary and Secondary Drinking Water Standards were examined as well as the ionic balance of key cations and anions (Bromwell and Carrier, 1987). EPA developed the Drinking Water Standards which represent the Maximum Contaminant Level (MCL) allowable (based on potential health concerns) and consist of numerical criteria 40 CFR Parts 141 through Part 143.

Results of laboratory analyses of chemical plants, various process waters indicate that ten constituents plus total dissolved solids (in terms of Primary and Secondary Drinking Water Standards) typically exceed EPA's Maximum Contaminant Levels (MCL). These constituents were utilized to define areas where seepage has affected groundwater quality and may pose a risk to human health.

Additional parameters were selected to model concentrations of "signature ions" (ions which are indicators of gypsum contamination) in ground water surrounding gypsum stacks. The ions selected were utilized to define areas of impact in the surficial and intermediate aquifer systems and also to model parameter concentrations within any process water seepage plumes. The USGS identified the following parameters listed below as dominant constituents in groundwater chemistry of acid seepage: alkalinity, calcium, chloride, fluoride, magnesium, sodium, sulfate, and potassium. The balance of these parameters and the percent increase in ionic concentration above background levels were used in calculations of ion indices to model the extent of influence from acid seepage on the local environment.

Surficial aquifer. Shallow surficial aquifers are the primary groundwater systems contaminated from phosphogypsum stacks (Bromwell and Carrier, 1987; Twachtmann, 1989). Data from groundwater monitoring at four sites were analyzed for impacts on the EPA Primary and Secondary Drinking Water Standards. Utilizing the exceedance distances tabulated for the seven Primary Drinking Water Standards evaluated, influence contours were developed for the model site and are depicted in Figure 4. Based on studies from four active phosphogypsum stacks, downgradient concentrations of selenium, silver, and fluoride attenuate very quickly and are less than the EPA MCL,s within 100 feet of the source. Downgradient concentrations of other constituents attenuate slower. Concentrations of lead and arsenic meet standards within 300 feet and 800 feet, respectively. Chromium and cadmium however, exhibited the greatest mobility within the surficial aquifer, requiring very long distances, up to 1200 feet, to fall below the drinking water standards.

The chemical constituents regulated by the Secondary Drinking Water Standards (iron, sulfate, manganese and total dissolved solids) exhibited much greater mobility. Analyses and modeling of the Secondary Standards was extremely difficult and limited greatly by the existing data base. Only two of the sites investigated had sufficient spatial distribution of groundwater monitoring wells within the surficial aquifer to enable approximation of a zone of impact. Due to the present data base limitation, it is impractical to model the attenuation of these parameters with a high degree of accuracy. However, there was sufficient data to approximate the following zones of downgradient impact:

> Exceedance Zone The area where EPA Secondary Drinking Water Standards are exceeded. This area is generally within 350 meters of the source.

Attenuation Zone The area where EPA Secondary Drinking Water Standards generally decrease in concentration and fall below the standards. This area will extend from 305 meters up to 610 meters at some sites and is highly dependent on site specific geologic and hydrology conditions.

Non-Exceedance Zone The area where EPA Primary and Secondary Drinking Water Standards are met. This area generally exceeds 610 meters and is also highly dependant on site specific geologic and hydrology conditions.

These zones are exhibited in Figure 5 as they relate to the model site,

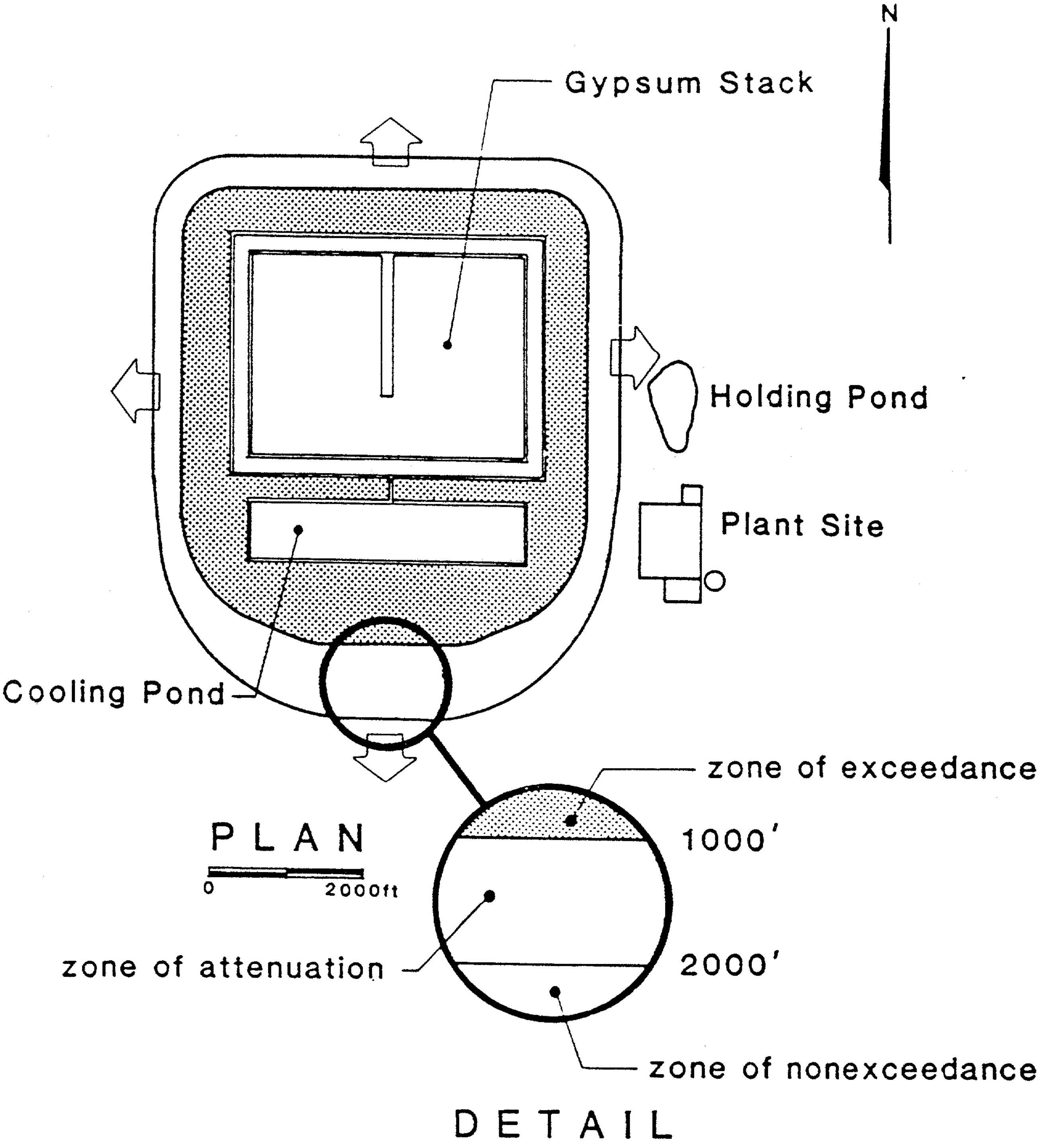
Intermediate aquifer. Bromwell and Carrier (1987) evaluated the available groundwater data base with respect to impacts to the intermediate aquifer. The evaluation was based upon both the EPA Primary and Secondary Drinking Water Standards. In all cases, Primary standards were not exceeded at any of the sites where data were obtained within the intermediate aquifer. Secondary standards of total dissolved solids, sulfate, and manganese were exceeded in only one well. The Twachtmann, (1989) Florida DER report stated that three of eleven active stacks are currently violating primary or secondary standards in either the intermediate or Floridan Aquifer.

The confining clay beds of the Hawthorn Group within the Central Florida Phosphate area have a high attenuation capability and tend to reduce concentrations of process water constituents to below EPA Primary and Secondary Drinking Water Standards. Impact from acidic leachate of phosphogypsum stacks within the intermediate and Floridan aquifer are reduced because of thick confining clay beds and high water flow rates, however, impacts are probable in areas where the confining beds are either discontinuous or absent, or a major breach occurs in a confining bed, such as from the result of a sinkhole forming (Bromwell and Carrier, 1987, Miller and Sutcliffe, 1984; PEI, 1986; Wissa and Fuleihan, 1985 Rouse and Bromwell, 1983).

MITIGATION OF ENVIRONMENTAL CONTAMINATION

Current rules, policies and regulations, such as NESHAPS 1989, and Florida Policy (Twachtmann, 1989) function to reduce environmental impacts associated with phosphogypsum stacks. There are, however, many sources of environmental contamination that can be reduced through appropriate mitigation techniques. The following sections of this chapter highlight mitigation concepts that reduce environmental degradation associated with phosphogypsum stacks.

Prior to the NESHAPS (1989) rule, phosphogypsum was utilized as a calcium sulfate resource. Active phosphogypsum use reduced accretion rates, but increased potential environmental contamination by radionuclides. Since the late 1920's, approximately five hundred million tons of phosphogypsum have been produced and accumulated as a waste by-product during the manufacturing of phosphoric acid in Florida. The Florida DER (1980)



NOTE: ARROWS INDICATE SEEPAGE FLOW

SOURCE BROMWELL AND CARRIER, INC , 1987

APPROXIMATED IMPACT ZONE: SECONDARY DRINKING WATER STANDARDS

FIGURE 5

estimated in the 1980's that all types of phosphatic wastes occupy approximately 70,000 acres of surface impoundments in the the Central Florida Phosphate District. Phosphogypsum stacks currently (1989) cover only a small amount of total acreage, approximately 5,000 acres.

Marketable uses of phosphogypsum separate into three categories: 1) agricultural applications, 2) construction materials, and 3) chemical raw materials. In agriculture, phosphogypsum can be used as a soil amendment to correct sodic conditions (Keren and Shainberg, 1980; Mishra, 1980), to reduce rainfall runoff and achieve better soil conservation (Miller et al., 1986), and as an effective way to ameliorate subsoil acidity (Sumner et al., 1986). Phosphogypsum is primarily composed of hydrated calcium sulfate, and as such it is an excellent source of both the calcium and sulfur needed for plant growth. Unlike lime it provides calcium without raising the soil pH and due to the low solubility of phosphogypsum, a single application can provide a long-term calcium supply. Sulfur in phosphogypsum is in the sulfate form which is readily available to a plant and does not require bacterial action to convert it to a form that the plant can utilize. The low solubility of phosphogypsum has another value: leaching due to rainfall is minimized. Sulfur deficiency in soils is widely recognized as a very common cause for reduced agricultural production. The benefits of phosphogypsum applications has been reported for studies on land reclamation (Merrill et al., 1980), in irrigated agriculture (Oster, 1980), on North Carolina crops (Baird and Kamprath, 1980), on Florida crops (Fitts, in press), for forage (Mullins, in press), and on citrus (Nemec, in press). Phosphogypsum has been used as a fertilizer for peanut crops in North Carolina and Georgia for many years (Lloyd, 1985).

The primary problems associated with using phosphogypsum as a soil amendment are the possible increase in background radionuclide content (Roessler, 1986; Guidry, 1986) and the cost of shipping phosphogypsum as a wet fertilizer. Guidry (1986) concluded that risks associated from eating vegetables grown on soils enriched with phosphogypsum would be low. Roessler (1986) provides estimated additions of Ra-226 to Florida soils based on established application rates.

While phosphogypsum is used internationally in wallboard and other building products, it is unlikely that it will ever be able to economically and environmentally compete with natural gypsum for these applications in this country. In North America, Sene Consultants (1987) concluded that the use of unpurified phosphogypsum for the construction of interior wallboard should be discouraged because of significantly increased indoor radiation exposure. Chang et al., (1989) demonstrated that phosphogypsum can be used as a road base in secondary roads at considerable savings over conventional materials. It is ideally suited for use as a base for parking lots. The Florida DOT has conducted laboratory scale testing on use as a fill material for roads, overpasses, etc. and supports field testing of this concept. Detailed civil engineering information can be found in volumes such as the Proceedings of the First International Symposium on Phosphogypsum (1980), Proceedings of the Second International Symposium on Phosphogypsum (1986), and Reclamation, Reconstruction, and Reuse of Phosphogypsum for Building Materials.

Possible environmental impacts associated with using phosphogypsum in road building include human exposure to radionuclides and long-term leaching of toxic contaminants. In addition, the potential exists for future human exposure, should roadbase material be reutilized. Ongoing studies sponsored by FIPR are currently evaluating environmental impacts associated with using phosphogypsum in road construction in Polk and Columbia Counties, Florida, although additional studies are currently precluded by the NESHAPS (1989) rules. The experimental projects call for a thorough environmental impact investigation which includes the pre- and post-construction sampling of air, soil and groundwater, including drinking water.

Phosphogypsum can also be thermally processed to produce SO_2 for sulfuric acid manufacture and CaS to be used as a means of elemental sulfur recovery (Wheelock et al., 1986; Kuehle and Knoesel, 1986; Clur, 1986; Kendron and Lloyd, 1986; Slinger, 1986; Gruncharov et al., 1986; Regin and Brooks, 1986; May et al., 1986). To date, the only processes that have shown potential for U.S. utilization have been those that produce SO_2 for sulfuric acid. The advantages of such processes are reduced manufacturing costs and a closed circuit system that minimizes waste (sulfur is converted into acid and phosphogypsum can be a constituent of cement).

SITE SPECIFIC MITIGATION

Dust generation can be controlled on the working surface, access roads, and side slopes to reduce the particulate emission rates. The natural crusting and vegetating of phosphogypsum stacks tends to reduce particulate emissions. The effectiveness of this mitigative action can be increased by engineered erosion control measures, such as hydroseeding, seed/nutrient matting, silt fencing, berming, and piping.

Disturbance of dried phosphogypsum can be controlled by proper planning of site operations, including minimizing disturbances and enhancing crust formation or by watering exposed surfaces. It may also be possible to locate and design the stack to minimize the erosion forces of the prevailing winds. These mitigative actions are also reported to have some effect on radon-222 gas, but not on gamma radiation.

The zero-discharge concept includes the design of a phosphogypsum stack system which does not include a surface water point source discharge of plant process/cooling water or free water drained from the phosphogypsum. An idealized zero-discharge system would include a system of dikes and ditches surrounding the entire phosphogypsum stack system.

A rim ditch and dike is constructed at the top of the working stack to contain the settling pond water, promote evaporation, improve the water balance and prevent surface run off. A cooling canal is constructed at the toe of the phosphogypsum stack to circulate process/cooling water from the chemical plant and also to intercept surface runoff and subsurface lateral flow from the phosphogypsum stack. The canal flows around the phosphogypsum stack, through a cooling pond and is returned to the chemical plant for reuse. The zero discharge system may also include a seepage ditch at the outer toe-slope of the process/cooling water canal. The water level in this ditch is maintained at a level lower than the ambient surficial groundwater by pumping. The pump discharge is directed to the process/cooling water canal. The pumped discharge includes seepage water from the phosphogypsum stack as well as fresh surface water and surficial groundwater from the surrounding area as makeup water for the chemical plant.

The design of all phosphogypsum stack ponds canals and ditches should include adequate freeboard to contain at minimum a 25 year/24 hour rainfall event. Spillways should be designed to direct excessive flows to an emergency holding pond. All dike and stack slopes should be designed for slope stability to minimize the possibility of failure and the release of impounded stack system waters to the natural surface drainage system.

Many of the techniques discussed above for surface water impact mitigation also provide mitigation for ground water impacts. However, the maximum protection of groundwater resources is provided by a combination of impervious vertical and horizontal barriers surrounding the phosphogypsum stack system.

Lateral leachate can be limited by the construction of a perimeter slurry wall which provides an impervious barrier at which point leachate can be ponded (subsurface) and/or captured by pumping for recirculation. This vertical slurry wall can be either continuous to the depth of a impervious horizontal strata, producing a subsurface ponding; or it can terminate in pervious strata, at which point recovery wells can capture the leachate by pumping. By pumping a positive pressure on the down-gradient side of the slurry wall and a negative pressure on the up-gradient (stack side), fresh surficial groundwater can be added to the cooling canal.

The most effective means of vertical subsurface seepage control is the use of a horizontal impervious strata beneath the phosphogypsum stack. This can be accomplished by either a man-made barrier of impervious synthetic or natural soil materials; or by siting the stack over a naturally occurring impervious geologic strata. In either case, a seepage collection and recycling system would provide the maximum groundwater protection. Either approach requires extensive geotechnical and geohydrological site investigations and testing to ensure proper design and operation.

A dewatering drain system can also be used under the working surface of the phosphogypsum stack. These drains are primarily used to promote drainage during low settling pond water periods (low rainfall), but they also provide another means of seepage control.

Phosphogypsum stacks should not be located in areas of known geological instability or where the surficial or intermediate aquifer is in direct contact with the Florida Aquifer. In addition, problematic areas to avoid include areas proximate to drinking water wells and areas prone to sinkhole formation. Conversely, areas more suited to stack siting, would be areas where thick natural confining layers are present, sinkholes are rare, and the geologic units have low permeability rates. A risk assessment for geological stability should be performed.

Land use mitigative measures can address conflicts that may arise due to past, current and future land uses. This includes human occupation, historical, archaeological, recreational and biological land uses. It may also be possible to protect some conflicting land uses by making design changes. For example, a significant archaeological site could be saved by excavation or possibly avoided by changing the shape of the phosphogypsum stack.

One demonstrated mitigation procedure is simply the establishment of a buffer zone surrounding the phosphogypsum stack. Environmental contamination and potential human exposure will be reduced as the buffer zone area increases. A 800 m buffer zone, especially if planted in long-lived, evergreen tree species, would reduce potential human health risks associated with phosphogypsum stacks.

CLOSURE REQUIREMENTS

Mitigation of post-operational impacts are best addressed by establishing phosphogypsum stack closure requirements. Closure should be implemented in a manner that will control, minimize and eliminate the post-operational escape of environmental contaminants while minimizing the need for post-operational maintenance. Phosphogypsum stacks will be closed in place unless future technology or market conditions make it feasible to handle such large quantities of material under applicable laws and regulations.

The basic requirements of a closure plan include: 1) prevention of contamination migration from the stack via air, groundwater and surface water; 2) control of surface water on the stack; and 3) maintenance of the stack integrity. Flexibility of these basic requirements is required to account for site-specific conditions.

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RADON EMANATION FROM ROADS CONSTRUCTED WITH PHOSPHOGYPSUM AGGREGATES

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ABSTRACT

This study was conducted to provide data for assessing the radiological impact from use of phosphogypsum (PG) as an aggregate material for applications such as road bases, parking lot bases, and embankments. Gamma, radiation and radon flux measurements were made at 11 test sections representing a variety of road configurations and base compositions incorporating PG or cement-stabilized phosphogypsum (SPG). Radon flux was also measured at two simulated embankments.

Gamma radiation levels reflected PG concentrations in the road base. Over sections with 100% SPG, the incremental levels were about 12 uR/hr, 2 to 2 1/2 times the vicinity background.

For blends. of PG or SPG with sand, gravel, and/or granite, radon emissions from the road base were proportional to PG content -- at nominal concentrations of 20, 40, and 80% PG, average radon fluxes were 1, 2, and 4 pCi/m^2-s, respectively. By contrast, emissions from sections with 100% SPG were on the order of 1 pCi/m2-s -- considerably less than projected by the trend for blends. Chip and seal paving provided little attenuation for the radon originating in the PG-containing road bases.

Radon emissions were in the range of 2 to 4 pCi/m^2 for the 0.6-m (24-in;) thick simulated embankments constructed of unblended raw PG or PG with 0.5% portland cement.

LIST OF SYMBOLS

pCi: picocurie; a unit of radioactivity.
1 pCi = 3.7 x 10^{-2} nuclear transformations per second.
PG: phosphogypsum.
SPG: stabilized phosphogypsum; 94% PG and 6% portland cement.
uR: microroentgen; a unit of gamma radiation intensity.

INTRODUCTION

Uranium and its decay series are associated with phosphate deposits of marine origin. Consequently, phosphogypsum (PG) produced in the wet-process production of phosphoric acid from such a phosphate rock source will contain the uranium descendent, radium-226, and its radioactive decay products.

One significant feature of radium-226 is that it is the constant production source of the radioactive gas, radon-222, which is emanated from radium-bearing materials. While the element radon is a noble gas and not very reactive chemically or biologically, it can reach the atmosphere. The radioactive decay of radon in the atmosphere results in the production of airborne short-lived radon decay products or “progeny”. Airborne radon decay products in sufficiently high concentrations have been associated, with lung cancer in underground miners and it is presumed that exposure to lower concentrations also presents a proportionate risk.

Radium-226 is ubiquitous in nature. Average concentrations in soil in the United States are on the order of 0.5 to 1.0 pCi/g; but levels vary and there are numerous instances of both naturally-elevated and technologically-enhanced concentrations. PG derived from Central Florida phosphate rock contains radium-226 concentrations on the order of 20 to 30 pCi/g.

This study was initiated in 1987 with the realization that the assessment of potential radiation exposure is an important prerequisite to the use of by-product PG for productive purposes. It was conducted on behalf of the Mobil Mining and Minerals Company of Pasadena, Texas, to develop data for use in assessing the radiological impact of the use of PG as an aggregate material for applications such as road beds, parking lot bases, and embankments.

Subsequent events have reinforced the importance of developing the data necessary for such an assessment. Emission standards for airborne radionuclides recently issued by the U.S. Environmental Protection Agency (EPA) require that PG, once produced, be disposed in stacks or mines (USEPA, 1989) and thus implicitly prohibit further use of this material. It was explained that this ruling reflected EPA’s concern that other uses of PG might result in numerous and diffuse radon sources that would present a public health threat (USEPA, 1990). At the time of this writing (May 1990), EPA had announced a limited reconsideration of the section limiting placement of PG to disposal stacks or mines and had proposed several alternatives to the rule. One of the options proposed for consideration would allow alternative uses of PG for which permission had been received from EPA. Said permission would be granted upon finding that the proposed use is at least as protective of the public health as would be disposal into a stack or mine.

In this study, radium-226 content was measured in various PG products and comparison materials as an indication of the radon production source. To provide an indication of the potential for exposure by the external radiation route to construction workers and users of the road, gamma radiation measurements were made over 11 test road sections containing PG in the road base. During the period, June 1987 - June 1988, surface radon emanation was measured from the road bases of these test sections, from the paving of selected test sections, and also from two test pads simulating the use of PG or PG aggregate in embankments.

TEST SITES, MATERIALS, AND CONDITIONS

Measurements were conducted in the Houston, Texas, vicinity on 11 test road sections at two sites, designated Site T and Site P, and on two simulated embankments.

The test material consisted of either PG or stabilized phosphogypsum (SPG), a mixture of 94% PG and 6% portland cement. The test road bases were constructed with PG or SPG, either alone or in various blends with other aggregate materials such as sand, gravel, and crushed granite (see Table I).

Table I. Test Road Sections

Section	Con-structed	Base	Base Composition, Percent by Weight					Paving[a]
			SPG	PG	Sand	Gravel	Granite	
A. <u>Site T</u>:								
T-A	1987	7"	100%	(94%)	--			CS-2
T-B	1987	7"	25%	(24%)	75%[b]			CS-2
T-C	1987	7"	25%	(24%)	50%[c]	25%	--	CS-2
T-D	1987	7"	20%	(19%)	--	--	80%[d]	CS-2
B. <u>Site P</u>:								
P-O	1986	8"	100%	(94%)	--	--	--	ASPH
P-N	1987	8"	100%	(94%)	--	--	--	CS-1
P-A	l/88	8"	80%	(75%)	20%	--	--	CS-1
P-B	l/88	8"	40%	(38%)	60%	--	--	CS-1
P-C	l/88	24"	40%	(38%)	60%	--	--	CS-1
P-D	l/88	24"	20%	(19%)	35%	--	45%	CS-1
P-E	6/87	8"	20%	(19%)	35%	--	45%	CS-1

Notes:
a) Paving:
ASPH = Asphalt.
CS-1 = l-course chip & seal.
CS-2 = 2-course chip & seal.
b) Section T-B: Sand = San Jacinto River Sand (SJRS), coarse.
c) Section T-C: Sand = 20% SJRS + 30% fractured gem sand.
d) Section T-D: Granite = 25% 3/4" granite + 25% D granite + 30% granite screens.

ROAD SECTIONS

Four test sections were studied at site T, a portion of a newly-constructed road. The road bases for the tested sections were a series of different SPG blends. The road was surfaced with a two-course cut-back asphalt and granite chip seal ("chip and seal" pavement).

At Site P, measurements were made on seven test sections with road base formulations that included a blend of unstabilized PG with sand and gravel, SPG, and several SPG/sand blends. All the road sections, except one, were paved with a one-coat chip and seal paving. One section with SPG base, designated as the "Old" or P-O Section, was covered with asphalt paving.

TEST PADS (SIMULATED EMBANKMENTS)

The two pads, simulating embankments, were located on the Mobil Pasadena site. One pad (P-21) contained raw PG while the other (P-20) contained PG with 0.5% portland cement. The pads had been constructed by compacting the material in 0.2 m (8-in.) liftto a total thickness of 0.6 m (24 in.).

METHODS

RADIUM-226 OF MATERIALS

The radium-226 content of materials used in the road construction and of vicinity soil was measured by high resolution gamma-ray spectrometry. In this method, a portion of sample is weighed into a 0.5-L molded plastic marinelli beaker. The loaded beaker is sealed and stored at least two weeks to allow ingrowth of gaseous radon-222 and its short-lived decay products into equilibrium with the radium-226 precursor. At the end of the in-growth period, the sample is counted with a multichannel gamma-ray spectrometer (Ge detector). The concentration of radium-226 is calculated from the 295 and 352 keV gamma peaks of lead-214 and the 609 keV peak of bismuth-214.

GAMMA RADIATION

Gamma radiation was measured with a scintillation survey meter (Ludlum Instruments Co. Model 19 uR-meter) that had been previously intercalibrated to a pressurized ionization chamber (Reuter-Stokes Model RS-111) in a natural radiation field. Measurements were made with the instrument held approximately 1 m above the surface.

RADON FLUX

Radon flux was measured by the charcoal collector method. In this method, radon emanating from the surface is collected on charcoal cartridges (Mine Safety Appliances Model GMC respirator cartridge) mounted in loosely-capped 7.6-cm (3-in.) diameter standpipes. For soils, 20-cm long pipes with one sharpened end, were used with the sharpened end pressed into the radon-emitting surface. For road bases and pavements, 16-cm long flat-ended pipes were used with the pipe supported in a stand and the pipe end sealed to the surface with a generous bead of caulk. The radon collected on the cartridges was measured by gamma scintillation counting; the radon flux was calculated from the radon collected, the area of the collector, and the length of the collection interval with appropriate corrections for radioactive decay during collection, delay, and counting.

Three collectors were deployed at each location and the average of the three was presented as the results for each measurement. Collectors were deployed for periods of time ranging from approximately 24 to approximately 48 hrs.

The primary effort was directed towards measurement of radon emanation from the road base as an indication of the presumed upper limit to the radon emissions; thus, radon flux was measured over a portion of unpaved base at all of the test sections. At Site T (chip and seal paving), measurements were also made over the first paving course with the loose chips swept away. At Site P, pavement measurements were made over intact and cracked portions of the single asphalt-paved section (Section P-O) and over one of the six sections with chip and seal paving.

During some of the samplings, measurements were made of the radon flux from the soil adjacent to the respective road sections at a distance estimated to be on the order of 0.15 m (6 in.) from the edge of the buried PG base.

Comparison data were collected by sampling from one or more reference sites in the general vicinity of each of the two test locations but at least 9 m (30 ft) away from the roads and test pads. Also for comparison purposes, during some of the sampling periods additional cartridges were exposed to ambient air near each of the test roads.

At the initial deployment in June 1987 involving six of the test sections, collectors were deployed and retrieved by members of the University of Florida team and transported back to the University as part of airline luggage. On the other occasions, Mobil personnel deployed and retrieved the collectors and shipped them to the University for analysis.

RESULTS AND DISCUSSION

RADIUM-226 CONTENT OF MATERIALS

Radioactivity analysis results are summarized in Table II. The non-PG materials all had low radium-226 concentrations - values were quite low (0.2 pCi/g) in builders sand from a local source, 1 pCi/g or less in local soil and in the rock used in Site T chip and seal pavement and slightly over 1 pCi/g in the granite sample.

By contrast, raw PG had a radium-226 concentration of 22 pCi/g and the various PG aggregate samples had concentrations in the range of 18 to 22 pCi/g, reflecting a slight dilution by cement stabilizer and/or other low radioactivity constituents.

Table II. Radium-226 Content of Materials.

Sample	No. of Samples	Ra-226, pCi/g[a] Avg.(Range)
Soil	3	1.0 (0.8- 1.3)
Builders' sand	1	0.2
Rock from C&S[b]	2	0.6 (0.5- 0.7)
Granite	1	1.3
PG aggregate[c]	2	19.2 (18.2-20.2)
SPG (94% PG) rubble	2	21.5 (21.1-21.9)
Raw PG	1	22.1

Notes :

a) Concentration on a dry weight basis. PG and SPG dried at 60° $\pm$ 5^0 C according to ASTM d2216-80.

b) C&S Rock = Rock from chip and seal pavement at Site T.

c) Further details of composition not stated for these samples.

GAMMA RADIATION

The results of the gamma radiation surveys are presented in Table III. Exposure rates over the PG roads were slightly elevated over the vicinity background and roughly reflected the percent PG in the base. For 100% SPG, the incremental values were on the order of 12 uR/hr giving a total exposure rate about 2 to 2 1/2 times the 8 - 11 uR/hr vicinity background.

RADON EMANATION FROM ROADS

At Site T, road base and paving measurements were made on two occasions, June 1987 and October 1987; adjacent and vicinity soil measurements were performed only in October. At Site P, from two to five measurements were made at the various test sections during the period June 1987 through June 1988.

In general, results for individual sections showed considerable variability from sampling to sampling. Consequently, substantial replicaton with time is necessary to accurately define long-term average values and to provide the basis for definitive conclusions about trends and differences. For some test conditions, the data are limited - only selected combinations of material, thickness, and paving are represented and some sections were sampled as few as only two times. Consequently, some of the interpretations are necessarily tentative based on limited data.

Table III. Gamma Radiation over Road Sections with Phosphogypsum Bases

Section	PG Content	Base Thickness	Paving	Gamma. uR/hr	
				Total	Increment
Site T:					
T-A	94% (100% SPG)	7"	CS-2	20	12
T-B	24% (25% SPG)	7"	CS-2	10	2
T-C	94% (25% SPG)	7"	CS-2	10	2
T-D	19% (20% SPG)	7"	CS-2	11	3
Vicinity				8	--
Site P-West:					
P-O	94% (100% SPG)	8"	ASPH	22	11
P-A	75% (80% SPG)	8"	CS-1	20	9
P-B	38% (40% SPG)	8"	CS-1	19	8
P-C	38% (40% SPG)	24"	CS-1	18	7
P-D	20%	24"	CS-1	17	6
Vicinity				11	--
Site P-East:					
P-N	94% (100% SPG)	8"	CS-1	23	13
P-E	20%	8"	CS-1	16	6
Vicinity				10	--

Notes:

Paving:

ASPH = Asphalt.
CS-1 = 1-course chip & seal.
CS-2 = 2-course chip & seal.

Increment = Incremental exposure rate
= Measured value - vicinity value.

Radon emanation from PG-containing road bases

The test sections included a variety of combinations of conditions that might affect the radon flux. Base materials consisted of both PG (unstabilized) and SPG in a series of blends with sand, gravel, and/or crushed granite; several thicknesses of base were included. Consequently, the data were first examined in an attempt to determine which factors appeared to have a discernable influence on the radon flux and which data sets could be pooled for further analysis.

While the base at most of the test sections contained SPG, two of the test sections had PG without stabilizer. These sections had 0.2-m (identified hereafter as 8-in.) and 0.6-m (identified hereafter as 24-in.) bases of 20% PG blended with sand and crushed granite. Comparing the available measurements for PG and SPG bases of comparable thicknesses and PG contents indicates:

- Phosphogypsum (not stabilized), one section with 8-in base of 20% PG (Section P-E):
  Average of two samples = 0.9 pCi/m^2

- Stabilized phosphogypsum, one SPG section with 7-in. base of 19% PG (Section T-D) and three SPG sections with 7-in. base of 24% PG (Sections T-B, T-C, T-C'):
  Average of seven samples = 0.7 pCi/m^2.

There is little difference in average radon flux between the PG and SPG sections. However, there are a number of limitations to this comparison - there was only a single 8-in. PG section to be compared against four SPG sections, there was one 24-in. PG section but no comparable SPG section, there was a small number of samplings (2) for each section, and the PG and SPG sections were not sampled at the same time.

The road base at most of the test sections was on the order of 7 to 8 in. thick; however, a 24-in thickness was also examined at Site P for two of the aggregate blends. Comparing the radon flux for the two thicknesses of each of these formulations for the two sampling dates for which measurements were made for both thicknesses indicates the following:

Average Ratio, 24-in./8-in.:
- 20% PG (not stabilized),
  two pairs of measurements: 0.4
- 40% SPG, two pairs of measurements: 0.9

Of the four pairs of measurements, a higher value was observed for the thicker. bed in only one case. The average ratios suggest that increasing thickness from 8 in. to 24 in. does not increase the radon flux from the base surface.

Since, in the available comparisons, there was no discernable difference between the various test blends in the range of 20 to 25% PG and increasing the base thickness did not increase the radon flux, the data were grouped by nominal PG content for further analysis (Table IV). The average radon flux for the various test sections is plotted against PG content in Figure 1.

These limited data indicate that, for blends ranging up to 80% PG by weight, radon flux increases in proportion to PG content. In contrast, the average radon flux from the test sections with 100% SPG was 0.8 pCi/m^2 -- considerably less than would be projected by the trend for for blends. The observed values were more comparable to those observed for blends in the nominal 20% PG range. This suggests that in the blends, the sand, gravel, and/or crushed stone is providing void space to enhance radon emanation and transport.

Table IV. Summary of Radon Emanation from Road Bases vs. Phosphogypsum Content

Base Composition	N	Radon Flux, pCi/m^2-s Avg (Range)
A. Nominal 20% PG Blended with Sand, Gravel or Granite		
Summary of Measurements	11	0.7 (0.1-2.1)
Summary of Section Averages	5	0.7 (0.3-1.3)
B. Nominal 40% PG Blended with Sand		
Summary of Measurements	5	1.5 (0.1-3.2)
Summary of Section Averages	2	1.6 (1.3-1.9)
C. Nominal 80% PG Blended with Sand		
Summary of Measurements, one section	3	4.3 (0.9-6.4)
D. SPG, No Blending		
Summary of Measurements	9	0.8 (0.1-4.1)
Summary of Section Averages	2	0.8 (0.4-1.3)

N = Number of measurements or sections in summary.

Effect of pavement

Although the major emphasis was on measurement of radon flux from the road base, a limited number of measurements were also made of radon emanation from the pavement over the PG base. Radon flux from chip and seal pavement surfaces was measured at the two samplings conducted at the Site T test sections and at one sampling at the "New" section at Site P. For those samplings for which measurements were made for both surfaces:

Mean and range of Pavement/Base ratio:

- Eight pairs of measurements: 0.9 (<0.2-2.3)
- Avg. ratios, five sections: 0.9 (<0.4-<1.7).

On the average there was little difference between the radon flux from the base and from the paving surface; there was an indication of a possible slight attenuation by the paving.

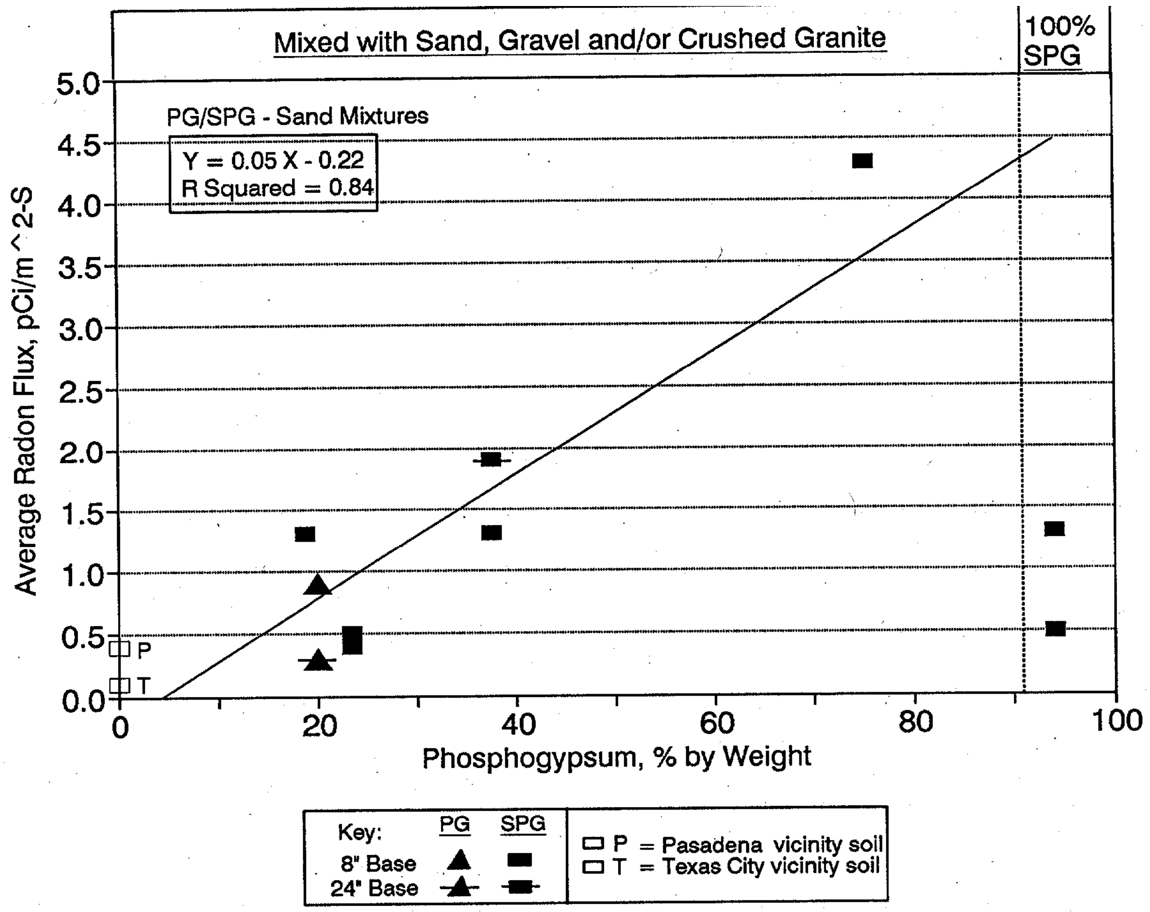

Figure 1. Radon Flux From PG-Containing Road Bases.

At the single test section with asphalt paving (the "Old" section at Site P), one measurement was made of the intact paving and two measurements were made over cracks in the paving:

Mean and range of Pavement/Base Ratios:
- Three pairs of measurements, one section:
7.5 (1.1-13.0).

The ratios all exceeded unity. This suggests that the asphalt paving itself contains radium-226 and constitutes a greater source of radon than the PG-containing base; however, no measurements were made of the radium content of the asphalt paving.

Effect on adjacent soil

Simultaneous measurements of radon flux were made at general vicinity soil reference locations, the soil adjacent to the road sections, and the road base during three of the samplings. Comparisons of the adjacent soil radon flux to the general vicinity reference locations are in Table V. For the various test sections with a nominal 20% PG, the adjacent soil values generally did not exceed the values for a reference location in the respective vicinity. At the two test sections with 100% SPG, the adjacent soil/general vicinity soil ratios were on the order of 1 to 2; several high values of adjacent soil/base ratio were observed when the values for the base were near the limit of detection. Although statistical testing was not performed, for these test sections the differences between the adjacent soil and the vicinity reference locations were probably not statistically significant.

At the sections with 40% and 80% SPG, the radon flux values for the adjacent soil were greater than the general vicinity reference value. This may be an indication of lateral movement of radon from the PG base into the adjacent soil, Alternatively, the origin of this radon may be irregular extension of the new base beyond the visible pavement, remnants of PG from the test section construction, or the underlying old PG road base (Sections P-O and P-A through P-D are built over an old paved road with a PG base). Because of the rather low flux values observed, the variation that occurs from sampling to sampling, the limited amount of sampling, and the possible mixture of materials present in the shoulder region, it is difficult to draw definite conclusions. In comparing the adjacent soil to the test road base, the average ratio, adjacent soil/base, ranged from 0.28 to 3.0 for the three sections tested. The lateral extent of the potential effect was not examined; however, any effect that occurs probably drops off rapidly with distance from the edge of the pavement. A conservative approach for modeling the radon source from roads would be to use a source width that is slightly larger than the specified base width.

RADON EMANATION FROM SIMULATED EMBANKMENTS

Sampling data are summarized, in Table VI. The average radon flux was on the order of 2 pCi/m^2-s for the pad containing raw PG and about 4 pCi/m^2-s for the PG with 0.5% cement. A paired-difference test applied to the four sets of data where both pads were sampled simultaneously indicated that the difference is not statistically

Table V. Summary of Radon Emanation from Soil Adjacent to Phosphogypsum-bearing Road Bases

A. Nominal 20% PG Blended with Sand, Gravel and/or Granite (Sections P-E, P-D, T-B, T-C, and T-D):

Mean Adjacent/Vicinity* Ratio	1.0
Range of ratios, 6 sets of measurements	(0.4->2.0)

B. Nominal 40% PG Blended with Sand (Sections P-B and P-C):

Mean Adjacent/Vicinity Ratio	9.8
Range of ratios, 4 sets of measurements	(3.5-16.0)
Range of average ratios, 2 sections	(8.2-11.4)

C. Nominal 80% PG Blended with Sand (Section P-A):

Mean Adjacent/Vicinity Ratio, one section	7.2
Range of ratios, 2 sets of measurements	(2.5-12.0)

D. SPG. No Blending (Sections P-O and P-N):

Mean Adjacent/Vicinity Ratios	1.4
Range of ratios, 4 sets of measurements	(0.6-3.0)
Range of average ratios, 2 sections	(1.1-1.8)

*Adjacent = Adjacent soil. Measurements immediately adjacent to the respective road section.
Vicinity = Vicinity Soil. Measurements at a sampling point, in the general vicinity of the respective test roads.

Table VI. Summary of Radon Emanation from Test Pads (Simulated Embankments)

Test Site	N	Mean (Range)		Std Dev	Std Err
P-21, Raw PG	4	1.8 +/- 0.9	(1.0-2.3)	2.1	1.0
P-20, PG + 0.5% cement	5	3.7 +/- 2.8	(1.6-6.9)	0.6	0.3
Pooled Data, P-20 + P-21	9	2.8 +/- 1.4	(1.0-6.9)	1.8	0.6
Bed-13, Existing Soil	5	0.3 +/- 0.4	(0.1-0.8)	0.3	0.1

N = Number of samplings in summary.
Mean is presented with 95% confidence interval.
Std Dev = Standard deviation of observations.
Std Err = Standard Error. the standard deviation of the mean.

significant at the 0.10 level. Pooling the data from the two pads gives a mean flux value of 2.8 +/- 1.4 pCi/m^2-s (95% confidence interval).

The mean radon emanation observed for the 0.6-m (24-in.) simulated PG embankments is intermediate between the 0.8 pCi/m^2-s observed for test section road bases of 0.2 m (8 in.) of unblended SPG and the 4 pCi/m^2-s observed for the road base test section containing a high SPG (80%) content blended with sand.

CONCLUSIONS

The results of this study lead to the following conclusions:

1. As would be expected from what is known about the radioactivity of phosphate rock and PG, PG aggregates have levels of radium-226 that are elevated above levels found in typical soils. Levels for the materials examined in this study were:

   Raw PG: 20 pCi/g
   Various PG aggregates: 15-18 pCi/g
   Granite: 1.2 pCi/g
   Other non-PG materials (local soil, builders's sand, rock from chip and seal pavement): <1 pCi/g.

2. Gamma radiation levels reflect the PG content (and hence radium-226 concentration) of the road construction materials. However, levels are not particularly high - over sections with 100% SPG, the incremental exposure rate was on the order of 12 uR/hr. This gives a total exposure rate on the order of 2 to 2 1/2 times the 8 - 11 uR/hr background for the vicinity of the test sites.

3. For comparable PG concentrations and empalcement under similar conditions, PG and SPG do not appear to differ in radon flux production: This is based on a limited number of comparisons.

4. Increasing the road base thickness from 8 in. to 24 in. does not appear to increase the radon flux from the base surface. This also is based on a limited number of comparisons.

5. The major factors affecting radon flux from the road base are a) whether or not the PG or SPG is blended with a granular filler material such as sand, gravel, and/or granite, and b) the PG content (and hence, radium-226 concentration) of the blend.

   - For blends up to 80% PG, the average radon flux increases in proportion to PC concentration. For nominal concentrations of 20%, 40%, and 80% PG, rounded average radon fluxes of 1, 2, and 4 pCi/m^2-s, respectively, would be expected.

   - For test sections with 100% SPG, a flux of approximately 1 pCi/m^2-s would be expected -- considerably less than would be predicted by the trends for blends.

6. Chip and seal paving provides little attenuation of the radon from the base; therefore, measurements on PG-containing road bases provide reasonable upper limit estimates of the radon flux from surfaces of roads with this type of. paving.

7. Average radon emanations from 24-in. thick embankments of PG or PG with 0.5% cement would be expected to be in the range of 2 - 4 pCi/m^2-s. This value is higher than the approximately 1 pCi/m^2-s observed for 8-in. test section road bases of unblended SPG and approaches the 4 pCi/m^2-s observed for the test section road base containing a high (80%) SPG content blended with sand.

The study left several questions unanswered:

1. The study did not determine whether asphalt paving has an attenuating effect on the radon produced by the road base. In a limited number (3) of paired measurements at the single test section with asphalt paving, the radon flux from the paving surface exceeded that from the bases in every case. This suggests that the asphalt paving contains radium-226 and constitutes a greater source of radon than the PG-containing base. Unfortunately, no measurements were made of the radium content of the asphalt paving.

2. There was limited, but inconclusive evidence that the radon flux from the adjacent soil is enhanced over the general vicinity reference value for blends with the higher PG concentrations (40 - 80% PG). Although distance effect was not examined, any effect that occurs probably drops off rapidly with distance from the edge of the road. A conservative approach for modeling the radon source would be to use a source width that is slightly wider than the specified base width.

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RADON DAUGHTER RISKS ASSOCIATED WITH PHOSPHOGYPSUM

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ABSTRACT

Current interest in environmental radon is driven by risk coefficients from uranium mining experience. It has been assumed that excess risk in uranium mining groups is accounted for by radon daughter exposures even though the miners were exposed to several other factors that could have contributed to the excess risk. Recent studies have investigated the possibility contributory effects of other factors in the mine environment. The studies should lead to better estimates of the risk coefficients for radon daughters only and thus to better estimates of risk due to environmental radon.

The radon daughter risks associated with phosphogypsum are low based on the uranium mining risk coefficients. The risks to the maximally exposed individual (upper bound risks) are on the order of 10^{-5}/year. The risk associated with radon daughters only is estimated to be one to two orders of magnitude lower than the uranium mining risk coefficients. Thus, radon daughter risks associated with phosphogypsum are probably de minimis ($<10^{-6}$/year).

INTRODUCTION

Although it has always been recognized that uranium miners are exposed to a complex atmosphere, lung cancer risk estimates are based on the assumption that radon progeny alone are responsible for differences between miners and control populations (Samet and Hornung, 1990). While such an assumption may be appropriate as a basis for occupational (miner) exposure guidance, it has not been shown to be appropriate as a basis for guidance for the general population. The general population is exposed (indoors) to different complex mixtures of chemicals and physical agents and to much lower levels in general. Also the general population is not exposed to some of the agents present in mine air.

Guidelines for general indoor and environmental exposures to radon daughters that are too low could be very costly. Such guidelines would be based on direct extrapolation of the uranium miner experience to derive guidance for the general population.

It is necessary to begin to examine in more detail to what extent the uranium miner experience can be used as a basis for general indoor exposure guidance. This paper begins to examine the many complex issues in a general way. Although no firm quantitative results can be offered, some important possibilities with respect to risk coefficients for environmental radon and directions for research are identified.

In this paper, we will show that doses due to long lived uranium daughters probably exceed doses due to short lived radon daughters in mine environments. The implications of this result with respect to risk coefficients for radon daughters alone are discussed. A comparison of the resulting risk coefficients for radon daughters alone with risk coefficients based on background radon daughter exposure and vital statistics on lung cancer results in good agreement.

RISK MODEL ILLUSTRATION

A recent National Academy of Sciences study by the Committee on the Biological Effects of Ionizing Radiation (BEIR IV, 1988) presented a new analytic model for lung cancer risk due to radon daughter exposures. The study considered the combined effects of smoking and radon progeny exposure on four mining groups. The possible effects of other contributing exposures or factors were not considered. The interaction of smoking and radon daughters appeared to be multiplicative. However, the model strictly applies to the four groups studied with their unique exposure conditions. The model did not lead to results that were substantially different from previous estimates of International Commission on Radiological Protection (ICRP), National Committee on Radiation Protection (NCRP), or United Nations Scientific Committee on the Effects of Ionizing Radiation (UNSCEAR) (see BEIR IV, 1988).

The most direct and simple approach to analysis of the effects of radon in a complex mixture is to assume linear, nonthreshold, additive exposure response relationships for all agents. Although such a far reaching assumption may not be generally true, the resulting model suggests results for radon daughter risk that are substantially different from current values. Current guidance is based on the same type of assumptions but with no assumed contribution from agents other than radon progeny and smoking.

Here we use a simple linear, additive formulation to illustrate risk in miners versus risk from radon daughters in the general environment. The total risk in the mining environment would be,

$$R_{TM} = R_B + R_R + R_{OM} \tag{1}$$

while the total risk to people in the general environment (nonminers) would be

$$R_{TE} = R_B \tag{2}$$

where R_B may include smoking, background radon, and other lung cancer causes in the general environment. RR represents risk due to radiation in mines and ROM represents risk due to other factors in mines (possibly arsenic, chromium, vanadium, etc.).

The excess risk attributable to mining is

$$R_{EM} = R_{TM} - R_{TE} = R_R + R_{OM} \tag{3}$$

In order to derive risk factors for radon daughters from the mining studies, the assumption has been made that REM is due to exposure to radon daughters only, that is

$$R_{EM} = K_{EM} \ E_{RM} \tag{4}$$

where ERM is cumulative exposure to radon daughters in working level months (WLM). Thus, K_{EM} represents the total risk coefficient for exposure in mine environments using radon daughters as a surrogate exposure measure. Walsh (1983) has shown that K_{EM} is approximately constant for 10 mining groups (~ 1%/WLM, 0.4-3% range). The National Academy of Sciences BEIR-IV Committee (BEIR-IV, 1988), using a constant relative risk model, provided estimates for the risk coefficients which ranged from 0.6 to 2.6%/WLM for the four mining groups studied. More recent analyses yield similar results (Samet and Hornung, 1990). Thus, in mine environments, the total excess risk is approximately proportional to cumulative exposure in WLM. Therefore, it is reasonable to use radon daughter exposures as surrogates for "dose" (risk α dose) in mine environments, although it is questionable as to whether all the excess risk is accounted for by radon daughter exposures alone.

Since exposures in the general environment do not include R_R and R_{OM}, use of K_{EM} along with radon daughter exposure in the general environment will likely overestimate risk due to radon daughters. Equation 3 and the empirical relation given in Equation 4 provides an expression relating radon daughter risks in mines to total risk,

$$R_R + R_{OM} = K_{EM} E_{RM} \tag{5}$$

where $R_R = R_{RM} + R_{UM} + R_{EX}$,

$R_{OM} = \Sigma R_i$

R_{RM} = risk due to radon daughters,

R_{UM} = risk due to uranium and long lived daughters,

R_{Ex} = risk due to external radiation, and

R_i = risk due to other factors such as arsenic, vanadium, silicon, nickel, diesel engine exhaust, etc.

In the linear, additive model the risk due to radiation is

$$R_{Ex} + R_{RM} + R_{UM} = K_{EM} E_{RM} - R_{OM}. \tag{6}$$

On the basis of a considerable body of radiation biology and dosimetry study, radiation risk is related to dose, D, in rem (see discussion in Walsh, 1979), thus

$$R_{RM} = K_{RM} D_{RM}, \tag{7}$$

$$R_{UM} = K_{UM} D_{UM}, \tag{8}$$

and $$R_{EX} = K_{EX}\ D_{EX}, \tag{9}$$

where K_{RM} = risk per rem for radon daughters,

K_{UM} = risk per rem for uranium daughters,

K_{EX} = risk per rem for external radiation,

D_{RM} = dose due to radon daughters (rem),

D_{UM} = dose due to uranium and long lived daughters (rem), and

D_{EX} = dose due to external radiation (rem).

Since by definition of dose equivalent as defined by the ICRP, the risk/rem for any type of ionizing radiation is the same (see Walsh, 1979), then $K_{EX} = K_{RM} = K_{UM}$. No similar concept has been developed for chemical toxicity and data on R_{OM} in miners is practically nonexistent. Combining Equations 6, 7, 8, and 9, an estimate of the risk coefficient for radon daughters only is

$$K_{RM} = \frac{K_{EM}\ E_{RM} - R_{OM}}{D_{RM} + D_{UM} + D_{EX}} \tag{10}$$

$$= \frac{K_{EM}}{DCF(RD)\ [1 + (D_{UM} + D_{EX})/D_{RM}]} - \frac{R_{OM}}{D_{RM} + D_{UM} + D_{Ex}}$$

where DCF(RD) is the dose conversion factor for radon daughters (rem/WLM).

If R_{OM} and the chemical effects of uranium ore dusts are ignored, an overestimate for K_{RM} will be obtained from Equation 10. Obviously, for a more quantitative estimate of K_{RM}, better information is needed.

In general, D_{EX} is expected to be only a small fraction of D_{RM} and will be ignored in the following discussion. A discussion of whether it is reasonable to ignore D_{UM}, based on a preliminary analysis, follows.

EXPOSURE IN URANIUM MINES

It is well recognized that uranium miners were and still are exposed to a highly complex environment. These exposures, when translated into dosimetric terms, would result in risk to the miners (R_{RM}, R_{UM}, R_{OM}, R_{EX}) in addition to background risks (R_B) that reflect background radon daughter exposures, other factors, perhaps smoking, etc. The analysis given here will ignore everything except exposures to radon daughters and uranium and long lived daughters (U-234, Th-230, Ra-226, Pb-210, Po-210). In effect, fewer factors will be ignored than is usually the case.

ORE DUST AND RADON DAUGHTERS CONCENTRATIONS

The dose due to long lived alpha emitters in ore dust has usually been ignored because the alpha activity in mine air from the short lived radon daughters is much greater than the alpha activity from long lived uranium daughters. Since U-238 has a long half life compared to all its daughters down to stable Pb-206, all daughters that do not migrate from where they are formed will be in secular equilibrium with U-238. That is, the activity of all daughters will be the same as U-238. Rn-222 and its daughters have a higher activity in mine air because radon is a noble gas and diffuses from the ore into the mine cavities. Rn-222 thus accumulates in mine spaces by diffusion and is removed by ventilation and radioactive decay. The short lived daughters of Rn-222 build up from Rn-222 and are removed by ventilation, radioactive decay and deposition on mine surfaces.

Sources of ore dust in mine air include cutting, drilling, blasting, and ore handling. In addition to ventilation, wet drilling and cutting techniques and water sprays are used to suppress dust in modern mines.

In 1980, the Bureau of Mines developed the Mine Inspection Data Analysis System (MIDAS) (Watts and Parker, 1987). MIDAS is a computerized, industrial hygiene data base collected in coal and noncoal mines and mills by Mine Safety and Health Administration (MSHA) inspectors or mine operators. MIDAS contains data collected since 1974 on respirable dust levels and radon in uranium mines. Respirable dust levels and radon levels reported by MSHA were taken in work areas thought to represent the highest probability for overpressure.

Geometric mean respirable dust levels in underground uranium mines were about 0.5 mg/m^3 with a geometric standard deviation of about 3 (Watts and Parker, 1987). Arithmetic mean concentrations were about 1 mg/m^3 with a standard deviation of about 3.5 mg/m^3. The U_3O_8 content of the ores in modern mines of the western U.S. is between 0.2-1% (DOE, 1979, Harley et al., 1981). The total alpha activity of natural uranium and long lived daughters is about 2 µCi/g Thus, 1 mg/m^3 of ore dust contains about 4-20 pCi/m^3 of uranium and long lived daughters. Arithmetic average radon concentrations were about 0.5 WL (D. R. Parker, personal communication, June 1990). The WL is any combination of radon daughters in one liter of air that will result in 1.3 x 10^5 MeV/L alpha emission. One combination of concentrations of radon daughters that satisfies the definition is 300 pCi/L which is approximately 3 x 10^5 pCi/m^3. Thus, 0.5 WL would be about 1.5 x 10^5 pCi/m^3 . The ratio of concentrations based on these values is about 2.7 x 10^{-5} - 1.3 x 10^{-4}. The values of

1 mg/m^3 for uranium ore dusts and 0.5 WL for radon daughters are used as representative values for modern mines from MIDAS. For more details on the MIDAS, the reader is referred to Watts and Parker, 1987 and the references therein.

Other estimates have been made for modern mines of the amounts of dust and radon produced per ton of ore mined (DOE, 1979). The concentrations of long lived uranium daughters in the dust relative to radon daughters can be obtained using the ratio

$$\frac{C_{UM}}{C_{RM}} = \frac{mfSn}{M_O f_R f S (1+f_e)} = \frac{m\ n}{f_R (1+f_e)} \quad x\ 10^{-6} \qquad (11)$$

where

C_{UM} = concentration of uranium and long lived uranium daughters in mine air,

C_{RM} = concentration of short lived radon daughters in mine air,

m = mass of dust (g) released per metric ton (10^6 g) of ore mined,

M_O = 1 metric ton ore (10^6 g),

f = percent of U_3O_8 in ore,

S = specific activity of U-238 (0.33 μCi/g),

n = U-238 plus number of long lived U-238 daughters included (U-238, U-234, Th-230, Ra-226, Pb-210, Po-210 : total = 6),

f_e = fractional equilibrium of radon daughters (= 0.5 as a representative degree of equilibrium), and

f_R = fraction of radon released.

If it is assumed that 100% of the radon is released, we will obtain a value for the concentration ratio provided a reasonable estimate for m is in hand. One estimate for modern mining conditions is m = 50 g (DOE, 1979). Thus, under the assumption of 100% radon release and 50 g dust per metric ton of ore mined (5×10^{-5} fractional release), the activity concentration ratio is 2×10^{-4}. All the 50 g of dust released will not be respirable. If about 25% of the dust is respirable, then the relevant concentration ratio becomes 5×10^{-5}. These low concentration ratios are the major reason, in addition to Equation 4, that uranium dusts have been ignored. However, the concentration ratio is generally not the risk-related dose ratio. That is, the dose ratio can vary widely for a given concentration ratio. A major research need is more complete information on dust levels and dust composition in mines. The dose ratio D_{UM}/D_{RM} is discussed in the next section.

In the early days of uranium mining, exposure levels were much higher for both radon daughters and ore dust. The U_3O_8 percentages in the ores were higher - up to 5% in western uranium mines compared to about 0.2% in modern mines. Dust levels in modern mines may be relatively lower because water is used for dust suppression in addition to high ventilation rates for both dust and radon suppression. Total particulate concentrations rather than respirable dust concentration were measured in the 1940s and 1950s and there is not enough information with respect to composition and particle size to directly convert from total particulate counts to respirable dust concentrations. Limited information that is available indicates that particulate concentrations up to 100 million particles per cubic foot (3.5 x 10^9 p/m^3 = 3.5 x 10^3 p/cc) and total mass concentrations up to 20 mg/m^3 were not uncommon (PNL 1974, George and Hinchcliff, 1971).

Note that 10^8 p/f^3 is about 3.5 x 10^3 p/cc which is not an unusually high concentration. In dose calculations for radon daughters, particle concentrations of 10^4-10^5/cc were assumed for "typical" mine atmospheres (Walsh, 1970). Raghavayya and Jones (1974) measured condensation nuclei concentrations from 1 x 10^3/cc to greater than 1 x 10^8/cc. The median concentration was 1 x 10^5/cc.

A series of experiments in the 1970s (PNL, 1974) used 4% cornotite ore dust that had a geometric mean particle size of about 1.2 microns and a geometric standard deviation of about 2.4. Concentrations in the exposure chambers were about 18 mg/m^3 at a particle concentration of 5 x 10^9/ft^3. Exposures to dust concentrations of 15 mg/m^3 containing 2% U_3O_8 dust are not thought to be unusual for early mines. The activity concentration corresponding to these values is about 600 pCi/m^3. Adequate data are not available to describe the average and spread of the data.

In the early mining experience, radon daughter concentrations of 10 WL were not uncommon. The activity concentration corresponding to a 10 WL total concentration is about 3 x 10^6 pCi/m^3. Thus a representative value for the ratio of the concentration of long lived uranium daughters to short lived radon daughters for early mines is 600/3 x 10^6 = 2 x 10^{-4}.

DOSE CONVERSION FACTORS FOR ORE DUST AND RADON DAUGHTERS

Dose conversion factors (DCFs) for radon daughters have been discussed extensively (see Walsh, 1983 for further discussion and references). The authoritative body on DCFs for all other radionuclides is the ICRP. Up until recently, the ICRP has considered radon daughters to be a special case and has not included DCFs for them in their recommendations.

However, Walsh (1979) and Jacobi (1973) have shown that the ICRP lung model (ICRP 66) provides a reasonable basis for radon daughter dose calculations. Dunning, et al., (1978) discuss the methods in more detail and provide estimates for radon daughters based on the ICRP model. Eckerman, et al., (1988) have provided updated calculations recently and the latest ICRP recommendations are contained in ICRP 30. The ICRP DCFs generally relate to average dose to whole lung or tracheobronchial tree (TB) region. Another impetus for reinvestigating the contribution of uranium and long lived uranium daughters is that the DCFs for insoluble compounds are significantly higher than they were 20 years ago. Because cancer in uranium miners primarily occurs in the TB region, and more frequently in the proximal airways than in distal airways, more detailed calculations have been attempted for radon daughters. Harley, et al., (1981, 1984) have provided dose estimates for long lived radionuclides in modern mine environments which indicate that doses to the bronchial epithelium may be comparable for long lived and short lived activity in mine environments. In this paper, the ICRP methodology will be followed.

Dose conversion factors (DCF) for the long lived uranium daughters and the short lived radon daughters are given in Table 1. Values for the long lived uranium daughters given in Table 1 were taken from Eckerman, et al., 1988. The overall value for short lived radon daughters is based on a report by Dunning, et al., 1979. Dunning, et al., estimated an overall dose conversion factor for short lived radon daughters of 2 rem/WLM whole lung and 4 rem/WLM for the tracheobronchial tree based on the ICRP lung model. Since exposure at one WLM results in an intake of about 51 μCi, the DCF for radon daughters based on the ICRP model is 2 rem/WLM/51 μCi /WLM = 0.04 rem/μCi. The solubility (clearance) class for U-238, U-234, and Th-230 in ore dusts is expected to be Y since the predominant form of uranium will be U_3O_8 which is insoluble (Dunning, et al., 1979). The total pulmonary DCF for insoluble U-238, U-234, and Th-230 is about 3000 rem/μCi inhaled. More soluble Ra-226 and Po-210 make a relatively small contribution to the total DCF. The total pulmonary DCF for short lived radon daughters, primarily the alpha emitters Po-218 and Po-214, is about 0.04 rem/μCi as discussed above. Thus, the ratio of pulmonary DCF from the long lived uranium daughters to the pulmonary DCF for the short lived radon daughters is about 3000/0.04 = 7.5×10^4.

Based on dose to the pulmonary region of the ICRP lung model, the dose from long lived uranium daughters will be equivalent to the dose from short lived radon daughters when the concentration ratio is $1/7.5 \times 10^4 = 1.3 \times 10^{-5}$.

Given the concentration ratios estimated above for mine environments of 1×10^{-5} to 2×10^{-4}, the ratio of pulmonary doses is about 0.7 - 15 as a preliminary rough estimate. A representative estimate for the ratio for early mines is about 6.

Table 1. Dose conversion factors for the Uranium-238 (4N+2) series (rem/microcurie)

	Solubility Class			
Nuclide	D	W	Y	
U-238	1	52.5	984	
U-234	1.2	5.9	1103	
Th-230	-	59.6	1110	
Ra-226	-	59.6	-	
Rn-222				
Po-218				Short lived radon daughters =0.04, see text
Po-214				
Bi-214	-	0.045	-	
Pb-214	-	0.05	-	
Po-210	2.7	48	-	
Pb-210	-	1.2	-	

It can reasonably be concluded that doses to the whole lung due to the long lived uranium daughters are comparable to and probably greater than doses to the whole lung from short lived radon daughters in underground mines. However, since cancer in the miners occurred predominantly in the tracheobronchial tree, the dose to the tracheobronchial tree is more biologically relevant.

Dose to the tracheobronchial tree and regions thereof has been the focus of radon daughter dose calculations. Since radon daughters have a short radiological half life, the effective half life (biological and radiological) is approximately the same as the radiological half life. Thus, clearance from and residence time in various regions of the lung is dictated by radiological half lives. In contrast, clearance of the long lived uranium daughters is governed predominantly by the biological half life because the radiological half lives are relatively long. One consequence of these differences in half lives is that radon daughters deposited in the pulmonary region of the ICRP lung model will not make a significant contribution to TB dose due to clearance from the pulmonary region through the TB region. Long lived daughters could make a significant contribution to TB dose as they are cleared from the pulmonary region by that route.

According to the ICRP model, about 40% of insoluble materials deposited in the pulmonary region will clear through the TB region with a 500 day half life and about 40% will clear through the TB region with a 1 day half life. Since the activity leaving the pulmonary region must pass through every section, i, of the TB region, the dose, D_i, to each section will be

$$D_i = 0.4 \, D_p \frac{M_p}{M_i} \tag{12}$$

where D_P is the dose to the pulmonary region from the activity clearing by the particular route under investigation, M_p is the mass of the pulmonary region, and M_i is the mass of section i. The dominant contribution to the pulmonary dose is from deposition of insoluble U-238, U-234, and Th-230 that clears with a 500 day half life through the TB region. Thus, in the cases of insoluble materials, D is approximately the total dose to the pulmonary region. There will be a geometric focusing effect on the activity since it is moving from a larger surface area and mass in the pulmonary region to smaller surface area and mass as it passes through the tracheobronchial tree. Thus, the mean physical dose (1 rad = 100 ergs/gm) can be much greater to areas of the tracheobronchial tree than to the pulmonary region. However, the higher physical doses may be offset to some degree by lower biological effectiveness due to increasingly thicker bronchial epithelium as the activity moves toward the trachea and to much higher dose rates to smaller masses. Also, the dose rate effect may be further enhanced because the activity may not be spread uniformly throughout the tracheobronchial tree. It could be accumulated into streams or into much smaller volumes surrounded by mucus material. Hot spot phenomena could result where the carcinogenic effect per rad could be less than a more uniform dose. Adequate information is unavailable to assess the effect of such possibilities.

Based on radon daughter dosimetry and epidemiology studies which did not include the contribution to dose from long lived uranium daughters, Walsh (1979) estimated a quality factor, QF, for alpha particles closer to 4 than to the value of 20 incorporated into the whole lung dose conversion factors given above. However, neither of these QFs may apply for the long lived uranium daughters being cleared from the pulmonary region through the tracheobronchial tree. Thus, our comparisons must be based on physical rad doses at present.

Harley, et al., (1981) indicated that for 1µm particles, the dose to the tracheobronchial tree from particles cleared from the pulmonary region was about 10 times the dose from direct deposition during inhalation and exhalation. They did not report pulmonary doses so that direct comparison with the approach in this paper is not possible.

The dose to the pulmonary region from uranium and long lived daughters is about 150 rad/µCi. For purposes of illustration, doses to the pulmonary region and to the tracheobronchial tree will be calculated for a concentration of uranium and long lived daughters of 5 pCi/m^3, which is approximately equivalent to a 1 WL concentration of radon daughters based on pulmonary doses.

The concentration of 5 pCi/m^3 (11 dpm/m^3) is similar to that used by Harley, et al., (1981, 1984) for their dose estimates. They report about 200-300 mrad/yr average dose to generation 10 of the tracheobronchial tree for the long lived radionuclides each at a concentration of about 7 pCi/m^3. Their estimates result in a DCF for U-238 and U-234 of about 6 rad/µCi, a value very different than suggested by the ICRP model as discussed below.

A simplified schematic of the movement of uranium and long lived daughters and doses to the pulmonary region and tracheobronchial tree is given in Figure 1. The parameters given in Figure 1 are taken from the ICRP lung model as described by Dunning, et al., 1974. The dose to the pulmonary region was calculated by multiplying the intake rate (10 nCi/yr) by the dose conversion factor (0.15 rad/nCi). Mean dose to the tracheobronchial tree was calculated using Equation 12 where M_p = 1000 g and M_i = mass of TB region = 50 g. Mean doses to sections of the tracheobronchial tree could be much higher. However, more information on masses of the sections within the range of alpha particles and the nature of the flow of uranium and long lived daughters through them is needed before one could properly interpret the results.

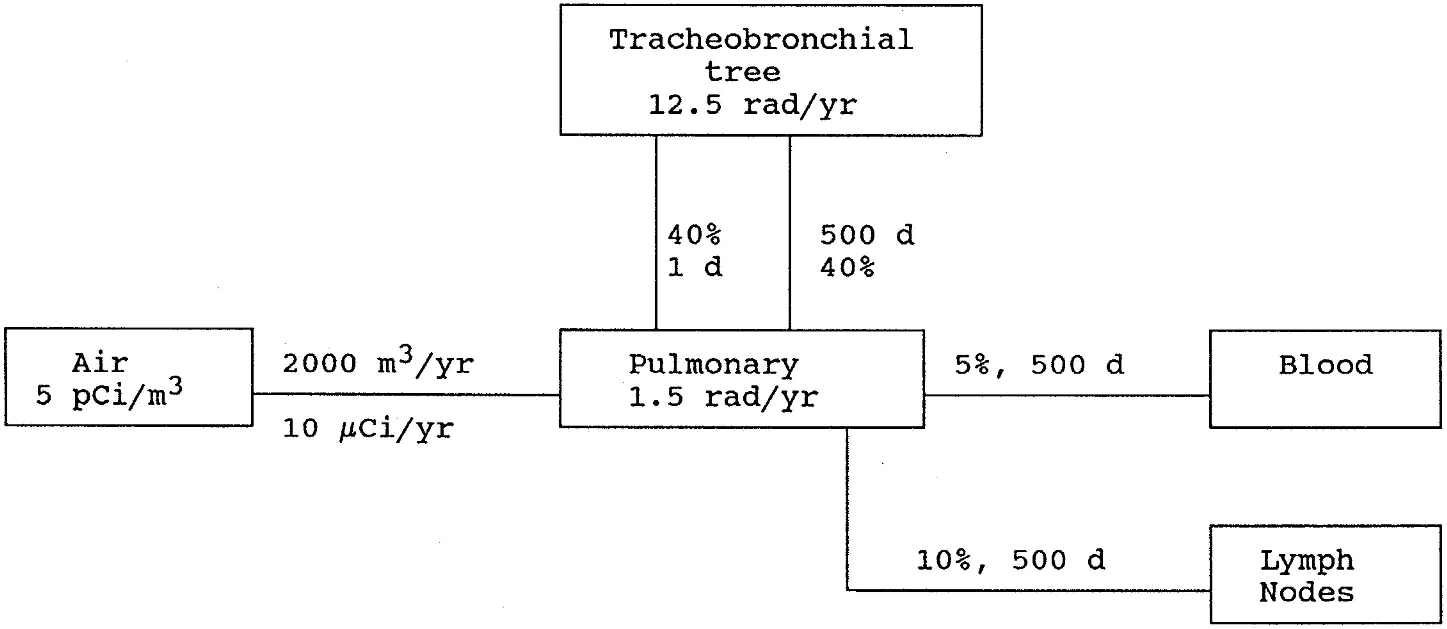


Figure 1. Schematic of the intake and clearance of insoluble materials from the lung as adapted from the ICRP lung models.

Since the pulmonary dose ratio, for a typical mine environment is about 6 and the ratio of tracheobronchial dose to pulmonary dose is about 8, the tracheobronchial dose ratio for the typical mine environment is about 48. More work is needed to assess the uncertainty in this preliminary estimate;

IMPLICATIONS FOR RADON DAUGHTER RISK

An expression for the risk coefficient for radon daughters only was given in Equation 10, which is based on a linear additive model. Considering only the possible effects of radiation dose from uranium and long lived daughters, the risk coefficient for radon daughters only in terms of excess relative risks/WLM (ERR/WLM) is,

$$K_{RM} = \frac{K_{EM}}{DCF(RD)\ (1 + D_{UM}/D_{RM})}. \qquad (13)$$

In Equation 13 D_{UM} and D_{RM} are doses in rem. The ratio of 48 for D_{UM}/D_{RM} estimated above was based on doses in rad. If we assume- that the rad to rem conversion factors are the same for alpha particles from uranium and long lived daughters and radon daughters, then $(1 + D_{UM}/D_{RM})$ -49. Since DCF(RD) for the tracheobronchial tree is about 4 rem/WLM, K_{RM} = 5 x 10^{-5}/rem in terms of excess relative risk per rem tracheobronchial dose. For the. pulmonary region, DCF(RD) = 2 rem/WLM and $(1 + D_{UM}/D_{RM})$ = 7, thus K_{RM} = 7 x 10^{-4} /rem. Using a weighting factor of 0.1 the excess relative risk per rem effective dose equivalent (EDE) is about 7 x 10^{-3}/rem.

For exposures to radon daughters only, the excess relative risk per WLM is 1.4 x 10^{-3}/WLM based on dose to the pulmonary region and 2 x 10^{-4}/WLM based on mean dose to the tracheobronchial tree.

The above values for excess relative risk per rad, rem, and WLM are preliminary values based on important assumptions. As discussed above, factors for conversion of rad to rem, the biologically effective dose, are not known in this context for either uranium and long lived daughters or for radon daughters. It is clear that, however, the risk coefficient in current use for indoor and environmental radon daughters may lead to significant overestimation of effects and thus to standards that are unrealistically low.

RISK COEFFICIENTS BASED ON VITAL STATISTICS

Risk coefficients for environmental radon daughters can be approximately derived without reference to the miner studies. The background incidence of lung cancer includes any contributions from environmental radon daughters. Vital statistics data are available that more directly include the radon daughter risk. The least confounded vital statistics data is that for nonsmoking females. However, readily available data for females includes a smoking contribution and these data will be used for this analysis.

One presentation of the data for females is given in Figure 2 taken from U.S. Cancer Mortality Rates and Trends, 1950-1979 published by the Environmental Protection Agency (EPA, 1987).

The age dependence shown in the bar chart is complicated but may be approximated up to age 70 by

$R_{aF} = K_F\ (a-30)$ for females

where $a \leq 70$ yrs and

$K_F = 1.72 \times 10^{-5}$/yr.

If a value for ERR/WLM were in hand, the risk due to background levels of radon daughters as a function of age, R_{RB}, a, would be

$$R_{RB}, a = \frac{ERR}{WLM}\ E_{RB}\ (WLM)\ R_a.$$

Since for background radon exposures the total exposure E_{RB} is the exposure rate $\dot{E}_{RB}$ times age, one may write for females

$$R_{RB}, a = 1.72 \times 10^{-5} \times \frac{ERR}{WLM}\ \dot{E}_{RB}\ a(a-30)$$

$$= 4.3 \times 10^{-6}\ \frac{ERR}{WLM}\ a(a-30)$$

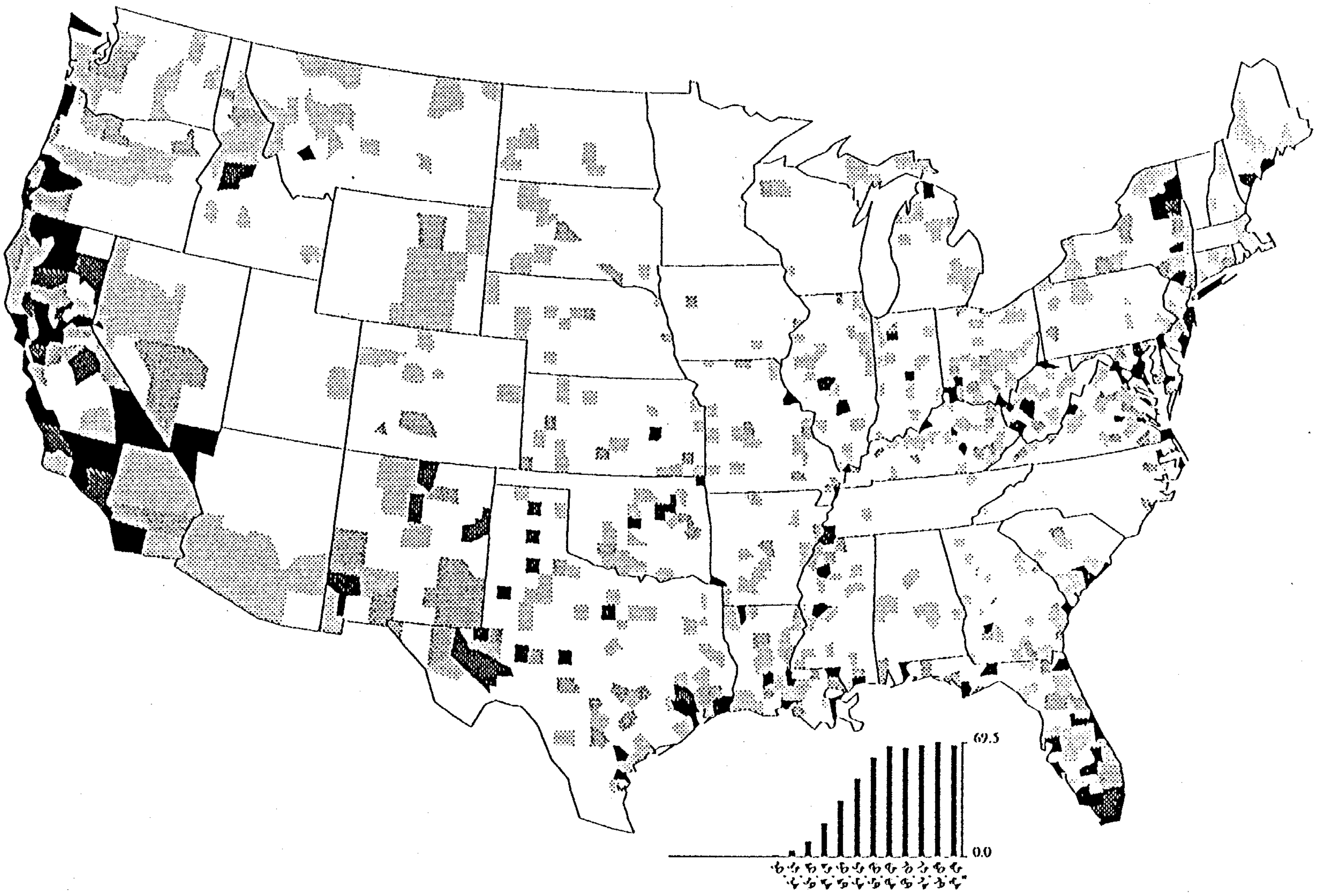
where $\dot{E}_{RB} \sim 0.25$ WLM/yr, for indoor exposures. (Walsh, 1983)

If ERR/WLM is not based on uranium miner studies, the dosimetry for radon daughters becomes crucial in order to relate to the total body of information on radiogenic lung cancer.

Dosimetry calculations based on the ICRP lung model indicate that the average dose to the tracheobronchial area of the lung is about 4 rem/WLM and about 2 rem/WLM to the pulmonary region (Dunning, et al., 1978). With a weighting factor of 0.1, the EDE is about 0.2 rem/WLM. Using an estimate of 2×10^{-4}/rem EDE based on ICRP, 1977, yields a risk per WLM of 4×10^{-5}/WLX. The resulting ERR/WLM for a lifetime$_3$ lung cancer background in females of -0.01 would be 4×10^{-3}/WLM This may be an upper limit estimate since it

Cancer of the Trachea, Bronchus and Lung including Pleura and Other Respiratory Sites

White Females: 1970 - 1979



ICD code(s): 162,163,165
by county

Figure 2. Taken from U.S. Cancer Mortality Rates and Trends, U.S. Environmental Protection Agency, 1987.

is based on linear, nonthreshold extrapolation for low linear energy transfer radiation.

From the previous discussion, the average value from the miner studies based on whole lung dose is about 1.4×10^{-3}/WLM According to the previous discussion, this value should also be considered an upper bound because other contributors in the mine environment were ignored. Thus, the two approaches are in reasonable agreement.

Using 0.004/WLM as the probable upper bound for ERR/WLM, we arrive at an expression for the contribution of background radon daughters exposures to background lung cancer

$$R_{RB,a} = 1.7 \times 10^{-8}\ a(a-30).$$

Based on this equation, the risk at age 70 due to exposure to radon progeny at 0.25 WLM/yr would be about 5×10^{-5}. The cumulative exposure in 70 years would be about 17.5 WLM. Thus, the excess risk per WLM would be about 2.7×10^{-6}/WLM. This result is about 37 times lower than the value normally used (1×10^{-4}/WLM based on uranium miner risk ERR/WLM -0.01 and lifetime lung cancer risk of 0.01 for a nonsmoker).

CONCLUSIONS

In this paper it has been shown that current mining risk coefficients significantly overestimate environmental radon risk. This result is based both on miner studies and independently, on vital statistics for background lung cancer combined with dosimetry for radon daughters.

Epidemiological studies at background radon levels are not likely to provide anything more than upper bounds for the environmental radon risk coefficients based on the power of the study. If the preliminary results given in this paper are confirmed by further study, epidemiological studies will be seeking to quantify a risk that is less than 5×10^{-5} in 70 years or 7×10^{-7}/yr.

Our quantitative results for uranium and long lived daughters and radon and short lived daughters are based on a specific set of assumptions and may not represent the values that will eventually be adopted. However, they are based on sufficient information to indicate that new directions in radon-related research are called for. These new directions would incorporate innovative approaches for accounting for probable contributors to lung cancer risk other than radon daughters in mine environments.

Accumulation of additional data from existing commercial mines and experimental mines will almost certainly be necessary in order to better characterize past exposures associated with the epidemiologically derived risks.

Dismissal of the possible contributions of agents other than radon daughters has been more a matter of professional opinion and the convenience of assumption for application of limited models rather than the result of careful, in-depth analysis.

The excessive costs that could be associated with radon regulation based on current mining risk coefficients is not justified if the basis of such costs are claimed to be excessive risk from radon daughters only. The money would be much better spent on a multitude of other more pressing needs.

Extreme conservatism in risk coefficients for toxic materials may appear to be the prudent, public health-biased thing to do. However, if these theoretical risk coefficients distract resources from areas of greater potential public health impact or inhibit the development and use of important technology, then much more harm than good is being done.

General research needs with respect to risk coefficients for environmental radon include risk assessment methods that treat complex mixture exposures in mining environments. In order to obtain a better estimate of the "true" radon daughter risk coefficient, ongoing studies must be broadened to consider other contributors to risk in mining environments. Systematic identification of uncertainties and research needs will allow better research funding decisions. Detailed radiation dose calculations for all radionuclides and development and application of assessment methods for non-radiological toxicants are vitally important.

The miner studies can be classic in the sense that they could allow us to learn much more about complex mixture exposures, dosimetry, and risks. That knowledge could change our perspective on radiation risks.

With respect to this symposium's purpose, the risk due to full time exposure at the maximum concentration location near a phosphogypsum field is about 1×10^{-7}/yr.

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POLLUTION LOADS FROM A LARGE CHEMICAL PLANT AND PHOSPHOGYPSUM STACK

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ABSTRACT

The paper defines the pollution loads flowing off in a controlled and an uncontrolled way from an industrial plant area into the Odra river and Szczecin Bay.

The presented investigations were carried out for Chemical Plant '"Police"'.

In the course of investigations it appeared that the amount of runoff pollution loads which so far has not been included in calculations is significant in relation to the amount of ultimate loads of contamination flowing from Ch. P. "Police" to the surface waters.

INTRODUCTION

Chemical Plant "Police" is situated to the north of Szczecin, about 45 km from Baltic sea. It cowers an area of 1300 ha (13 km^2) and produces mainly fertilizers.
From this total area, old part of the plant is covering 230 ha (2,3 km^2) and it is called Ch. P. “Police I”, new part of the plant is covering 460 ha (4,6 km^2) and it is called Ch. P. “Police II”. The rest of area 610 ha (6,1 km^2) is devoted for phosphogypsum stack, copperas stack ($FeSO_4 \cdot 7H_2O$), sewage treatment plant and other purposes.

Total employment amounts to about 4000 persons, who are working on three shifts. Beginning the production was in 1969.

CONTROLLED POLLUTION LOADS

Ch. P. "Police" is flowing off into Odra river and Szczecin Bay sanitary and industrial sewage as well as cooling waste water. These waste water are flowing off in a controlled way. The mixture of sanitary and industrial sewage is purificated on sewage treatment plant and after storage - settling tank flows off into Szczecin Bay (fig. 1). The cooling waste water flows off into Barge Channel and next into Odra Waski Nurt river (fig. 1).

The results of selected contamination loads in sanitary - industrial sewage and cooling waste water from Ch. P. "Police I + II" are shown in table I. Selected indicators of contamination such as phosphates (PO_4^{-3}), sulphates (SO_4^{-2}), fluorides (F^-) iron (Fe), ammonia nitrogen $N_{NH_4^+}$, chemical oxygen demand (COD), suspended solids (SS) and pH are characteristic for the realized production profile in Ch. P. “Police”.

The samples for measurements of contamination concentrations were taken by author in August - October 1987.

The flows were taken on the base of Water - Law Permission for Ch. P. “Police” November 30, 1984 confirmed by Polish Ministry of Environmental Protection (1988.12.15).

The samples of sanitary - industrial sewage were taken in point 4 (fig. 1) and samples of cooling waste water were taken in point M (fig. 1).

Table I. Selected contamination loads in sanitary and industrial sewage (index No 1), and cooling waste water (index No 2) from Ch. P. "Police" into Odra river and Szczecin Bay.

Indicator of contamination	Q_1 m³/h	Concentrations C_1 mg/l	Load $L_1=Q_1C_1$ kg/h	Q_2 m³/h	C_2 mg/l	L_2 kg/h	Q_{1+2} m³/h	L_{1+2} kg/h	Ultimate contamination loads for all sorts of waste water from Ch.P. "Police" (Water ..., 1984) Q m³/h	Load kg/h
1	2	3	4	5	6	7	8	9	10	11
PO_4^{-3}	7020	1,9÷12,8 2,0	14,0	12594	0,9÷11,8 1,0	12,6	19614	26,6	19614	13,8
SO_4^{-2}		1415÷2090 1800	12640		67 ÷128 70	880		13520		9684
F^-		10,8÷16,0 12,0	84,0		0,54÷1,9 1,0	12,6		96,6		166
Fe		0,07÷0,54 0,2	1,4		0,11÷0,30 0,2	2,5		3,9		19,5
$N_{NH_4^+}$		1,0÷2,4 1,5	10,5		0,2÷0,82 0,2	2,5		13,0		25,5
$COD-O_2$		47÷126 60	420		60÷118 60	760		1180		455
SS		7÷25,0 10,0	70		8,0÷21,0 10,0	125		195		515
pH		7,1 ÷ 8,4			7,2 ÷ 7,8					7,0 ÷ 9,0

UNCONTROLLED POLLUTION LOADS

The storm water drained to cooling water sewage system and flowing off in runoff from phosphogypsum stack are the sources of uncontrolled pollution loads.
At present these sources are the more dangerous for Odra river and Szczecin Bay than sewage flowing of in controlled way. Considering still enlargement of phosphogypsum stack this source of pollution loads is the most dangerous.

The investigations were undertaken due to the lack of comprehensive studies concerning the quantity and quality of storm water drained by industrial sewerage and flowing off in runoff from industrial wastepiles. The studies on urban runoff pollution in other industrial regions are more advanced (Toronto, etal, 1986).

From the scientific point of view it is interesting to compare the amount of loads of storm water. from industrial areas with the ultimate pollution loads determined for all sorts of waste waters drained into receiving waters.

RUNOFF FROM PRODUCTION AREA

Studies were limited to the old part of the plant covering 230 ha (2,3 km^2) called Ch. P. '"Police I", Storm waters are drained to cooling water sewage system and the mixture flows to an open canal for cooling and storm water discharge (fig. 1). The results are shown in table II, Selected indicators of contamination are characteristic for the realized production profile in Ch. P. "Police". $Q = 12300\ m^3/h$ was calculated on the use of such parameters: probability of rainfall $p = 50\%$ runoff coefficient $\psi = 0,3$, representative rainfall time $t = 38$ min, total average yearly rainfall for Ch, P. ‘Police” $H = 557$ mm and the watershed area $F = 230$ ha.

Concentration of contamination in column 3 was measured immediately after the rainfall. Samples were taken from tanks of the volume 20 l suspended on steel wires at street inlets to be found over the whole plant area. After each rainfall the samples were taken and the tanks were emptied. As these is no separate storm drainge system this measurement method had to be applied.

It enables an evaluation of the contamination of particular parts of the production area which is connected with the location of street rain inlets. Due to the lack of data from direct measurement of total loads of runoff pollution, minimum approximated calculations results there appears to be a threat of contaminating surface waters.

Table II. Pollution loads of storm water drained from production area of Ch. P. "Police I" to surface water.

Indicator of contamination	Q [m³/h]	Range of concentrations min - max [mg/l]	Concentration C [mg/l]	Load L=Q·C [kg/h]	Ultimate contamination loads for all sorts of waste water from Ch. P. "Police I"	
					Q [m³/h]	L [kg/h]
1	2	3	4	5	6	7
PO_4^{-3}		0,4 - 155	10,0	123		9,6
SO_4^{-2}		21 - 2130	300,0	3690		5058
F^-		0,36 - 7,2	1,5	18,5		83,1
Fe	12300	4,1 - 115	4,0	52,0	12971	13,6
$N_{NH_4^+}$		1,23 - 17,6	1,5	18,5		17,5
$COD\text{-}O_2$		116 - 2020	120,0	1476		307,0
SS		190 - 12480	320,0	3936		343,0
pH		4,0 - 9,6				7,0-9,0

At present the author is working out the results of yearly direct measurements (1988) of discharge and concentrations of cooling water and the mixture of cooling and storm water (point M, Fig. 1). They are connected with direct measurements of rainfall rate and concentrations of the same contamination indicators regarded as background (point D.1, fig. 1). Measurements concern the whole production area covering 690 ha, including also the new part of chemical plant called “Police II”.

RUNOFF FROM PHOSPHOGYPSUM STACK

One of the products of the Ch. P. "Police"' is phosphoric acid and phosphogypsum is its by-product (2,3 million tons per year - 1988). Dry phosphogypsum stack amounts to 34,4 million tons (up to 1988 and cover the area of over 100 ha (fig. 1), Further tons of phosphogypsum per year. At present less than 0,05% is being utilized annually. The investigations on phosphogypsum and its utilization are more developed in the U.S.A. (Chang, 1987), (Lloyd, 1985), (Nifong, 1988) - Australia (Beretka, 1980) - Canada (Collings, 1980) - Japan (Miyamoto, 1980) - Sweden (Wiberg, 1982) and in other countries.

The investigations were undertaken due to the lack of comprehensive studies concerning the quantity and quality of surface runoff from phosphogypsum stacks. Investigations on ground water pollution are more advanced, (Wissa, Fuleihan, 1985).

The presented paper is the continuation of investigations undertaken by the author few years ago (Rydzynski, 1988). On the basis of analytical and experimental research the algorithm of calculating the amount and quality of runoff from the phosphogypsum stack as the function of rainfall rate and stack parameters such as natural moisture, porosity and its. slope was defined.
Phosphates, sulphates, fluorides, iron, ammonia nitrogen, chemical oxygen demand, chlorides, suspension and pH were selected as characteristic contamination indicators.

As a result of analytical and experimental research work the following equations were used (Rydzynski, 1988):

$$q_s(t_1),\ C(t_1),\ L(t_1) = f(q,\ W,\ \beta,\ n,\ F) \qquad (1)$$

where:

$q_s(t_1)$ - discharge of surface runoff $[L^3T^{-1}]$,
$C^s(t_1)$, $L(t_1)$ - concentration and load of eroded phosphogypsum in the form of suspended solids $[M\ L^{-3}]$, $[M\ T^{-1}]$,
q - rainfall rate $[L\ T^{-1}]$,
W, n - natural moisture and porosity of stack at $t = 0$ [%],
t - runoff time [T],
β - stack surface slope [%],
F - protection area of stack $[L^2]$.

In order to determine the hazard of polluting Szczecin Bay by the runoff from phosphogypsum stack, the calculated loads were compared with ultimate contamination loads for all sorts of waste water coming from Ch. P. "Police" (tab. III).

Table III. Selected contamination loads in runoff drained from phosphogypsum stack.

Indicator of contamination	Range of contaminations min - max	q [m^3/h]	C [mg/l]	L [kg/h]	Ultimate contamination loads for all sorts of waste water from Ch. P. "Police"	
					Q[m^3/h]	L[kg/h]
1	2	3	4	5	6	7
PO_4^{-3}	11,0 - 15400	q = 61 l/sha	200	272		13,8
SO_4^{-2}	520 - 3600	W = 55 %	2000	2720		10680
F^-	0,6 - 51,0	n = 53 %	20	27,2		166
Fe	0,07 - 46,1	β_1 = 58 %	10	13,6	19614	19,4
$N_{NH_4^+}$	0,09 - 4,8	F_1 = 12,8 ha	2	2,7		25,6
COD-O_2	178 - 350	β_2 = 10 %	180	245		455
SS	45000 - 369000	F_2 = 13 ha	103000	140000		515
pH	1,8 - 6,4	β_3 = 0% F_3 = 62,2 ha $q_s(q,W,n,\beta,F)$ $\cong$ 1360				7,0 - 9,0

CONCLUSIONS

- In the course of investigations it appeared that the amount of runoff pollution loads which so far has not been included in calculations is significant in relation to the amount of ultimate loads of contamination from Ch. P. “Police’” to the surface waters.

- Studies proved that the load of phosphates especially in runoff from phosphogypsum stack which is the most essential indicator from the water protection point of view exceeds considerably the ultimate load of phosphates. for all sorts of waste water from Ch. P. "Police".
  The ultimate load of phosphates was determined to protect Szczecin Bay and Baltic Sea from eutrophication (Convention..., 1974).

- The existing pumping installation near the phosphogypsum stack is not sufficient.

- Works on project of water environment protection in the proximity of the phosphogypsum stack which is being realized by

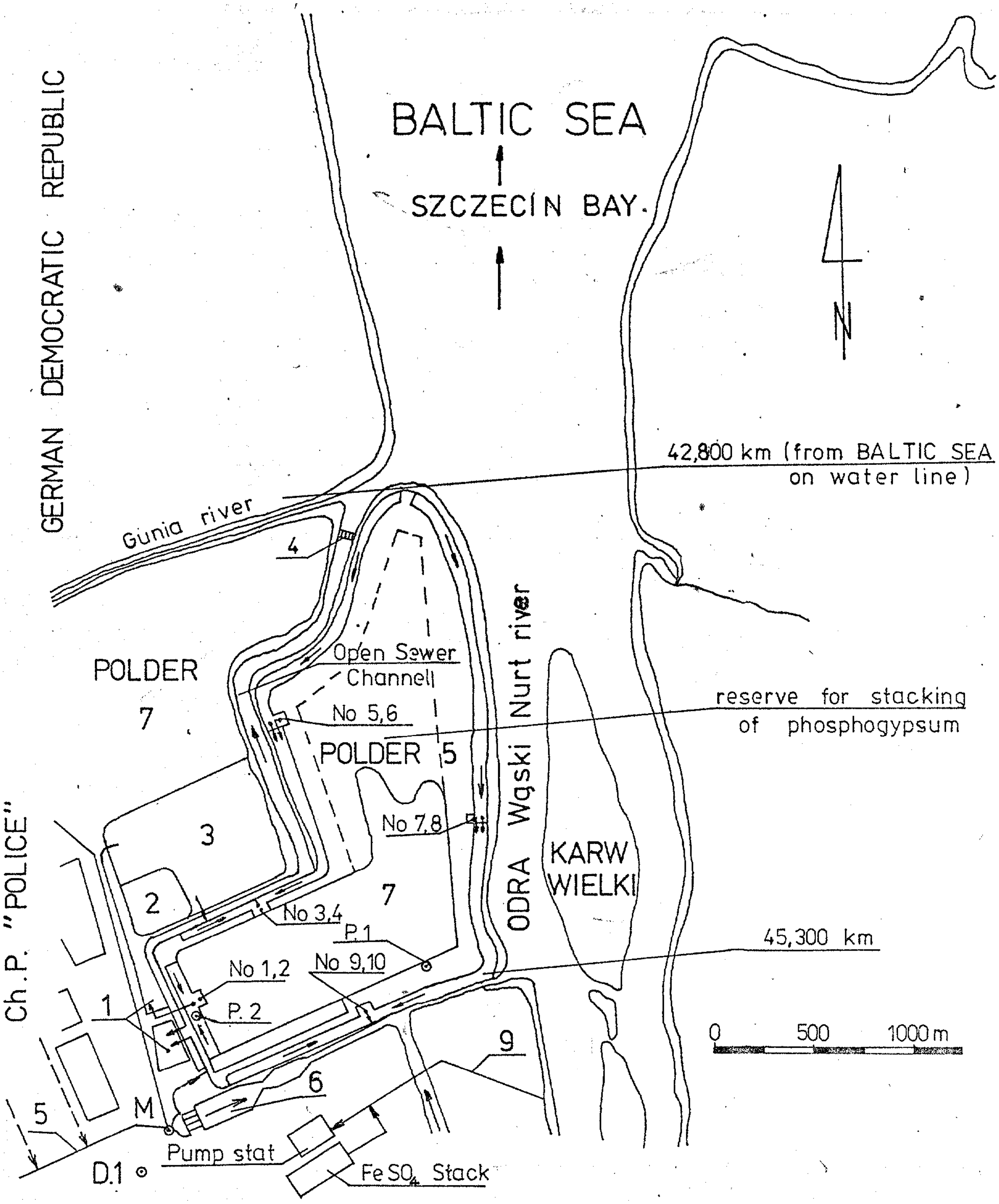

Fig. 1. Ch. P. "POLICE" Phosphogypsum Stack

1. Sewage Treatment Plant; 2. Lagoon; 3. Storage - Settling Tank; 4. Outlet 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;

P.1, P.2 - samples of water from stack; D.1 - samples of rainfall; M - samples of mixture storm and cooling water

No. 1 - projected dewatering of phosph. stack by means of FLYGT pumps

Szczecin Design Office “Bimor”, should proceed much quicker.

- At the same time proper stainless steel FLYGT pumps for dewatering phosphogypsum stack can be tested according to author's proposal (fig. 1).

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ENVIRONMENTAL IMPACT OF AIRBORNE RADIOACTIVITY EMISSIONS FROM A PHOSPHOGYPSUM STACK

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ABSTRACT

In anticipation of a two-phased expansion of the existing phosphogypsum stack at a phosphoric acid plant complex in the Central Florida phosphate district, radioactivity measurements were collected on and in the vicinity of the existing phosphogypsum stack. Radon exhalation from the surface of the phosphogypsum stack was measured at 45 sampling points. These measurements were used to develop radon source terms for various areas of the phosphogypsum stack. Ambient measurements of radon in the vicinity of the phosphoric acid plant complex were also collected in an attempt to evaluate the impact of the radon emissions from the stack on the radon concentrations in the general environment.

Using atmospheric dispersion modeling techniques, the radon emissions from the phosphogypsum stack were used to estimate ambient concentrations of radon at various receptor points in the vicinity of the phosphoric acid plant complex. In addition, estimates of radium-226 emissions in airborne particulate matter were made using particulate matter emission factors developed by the Environmental Protection Agency. Using these radium-226 emissions along with particle size distribution information for the phosphogypsum material, concentration estimates of airborne radium-226 in suspended dust and deposition estimates of radium-226 onto soils were made in the vicinity of the phosphoric acid plant complex.

INTRODUCTION

IMC Fertilizer, Inc. (IMCF) currently operates a chemical complex at its New Wales Facility in western Polk County Florida approximately five miles southwest of Mulberry. Part of this complex is involved in the production of phosphoric acid from phosphate rock. This process generates a byproduct known as phosphogypsum which consists primarily of calcium sulfate. Approximately five tons of phosphogypsum are generated for each ton of phosphoric acid produced. The gypsum is slurried and transported at approximately 20,000 gallons per minute to a pile or "stack" east of the plant where it is allowed to settle in settling compartments. The existing phosphogypsum stack covers a land area of approximately 430 acres. The storage of byproduct gypsum requires a volume of approximately 5200 acre-feet per year. The slurry which is used to transport the phosphogypsum to the top of the gypsum stack forms a pond which covers a substantial portion of the top of the stack. The current elevation of the existing gypsum stack is approximately 100 feet above grade and is expected to reach 200 feet above grade at its maximum height.

At the projected rate of phosphoric acid production, the existing gypsum stack is expected to reach a height of 200 feet above grade in May 1992. To continue operating the phosphoric acid plant beyond that time, IMCF must expand its gypsum stack. As part of the permits required to expand the existing gypsum stack, IMCF is required to submit an Application for Development Approval to the Central

Florida Regional Planning Council. This study was conducted in support of that application. The expansion of the existing phosphogypsum stack at New Wales will be staged to accommodate a variety of stack configurations.

Since phosphate rockcontains naturally-occurringuranium, radioactive components of the uranium decay series are associated with the phosphate material. In the production of phosphoric acid, radium-226 is co-precipitated with the phosphogypsum byproduct and remains with the stored phosphogypsum. Through the process of radioactive decay, radium-226 produces radon-222, a radioactive noble gas. Radon-222 in turn, decays to a series of radioactive decay products collectively known as "radon daughters" or "radon progeny". Quantities of radium-226 and radon-222 in the environment are typically expressed in picocuries (pCi). Radon daughter levels are commonly expressed in "working levels" (WL).

This radiological assessment has been directed toward quantifying (1) the source of potential radioactivity emissions from the phosphogypsum stack, (2) the emissions of radioactivity from the stack, and (3) the ambient concentrations of radioactivity in the environment surrounding the New Wales facility. Since phosphoric acid production processes are not expected to change during the life of the proposed stack, data collected for the existing stack can be used to project these parameters for the proposed stack expansion.

In this regard, samples of phosphogypsum were collected and analyzed for radium-226 to characterize the potential for its release to the environment from the phosphogypsum stack. Radon flux measurements were taken to measure radon emissions from the stack. Ambient concentrations of radon in air, working levels, and radium-226 in suspended particulate matter were measured to estimate concentrations of radioactivity in the environment surrounding the New Wales facility. In addition, atmospheric dispersion modeling techniques were used to estimate ambient concentrations of radon expressed in working levels.

ENVIRONMENTAL RADIATION CRITERIA

The U.S. Environmental Protection Agency recently adopted National Emission Standards for Hazardous Air Pollutants (NESHAPS) which limit emissions of radon-222 from phosphogypsum stacks to 20 picocuries per square meter per second (pCi/m^2-set). Standards for radium in ambient air or radium in soils have not been promulgated. However, other criteria do exist which can be used for comparative purposes.

The State of Florida maximum permissible concentration (MPC) for radium-226 in air is 2×10^{-l2} microcuries per milliliter or two picocuries per cubic meter (Florida Administrative Code, Chapter 10 D-91). This MPC is not an ambient air quality standard but refers to releases of radioactive materials by holders of Radioactive Materials Licenses. While no specific criteria exist for radium deposition, the National Council on Radiation Protection and Measurements has recommended a guide of 40 picocuries of radium-226 per gram of soil as a concentration to be evaluated for agricultural land use (NCRP 1984).

With respect to radon-222 progeny, the State of Florida has adopted an indoor standard of 0.02 WL (Florida Administrative Code, Chapter 10 D-91). For the purposes of comparing radon concentrations in air to this radon progeny standard, a concentration of 4 picocuries of radon in one liter of air is considered to be equivalent to 0.02 WL.

METHODOLOGY

Samples for the radiological assessment were collected from two types of sampling stations: on the phosphogypsum stack itself and in the environment surrounding the New Wales facility. Sampling on the stack was directed towards evaluating the potential for radioactivity releases from the stack. Most of these sites are located near the roadways on top of the stack; some sites are located on the sides of the stack. Additional sites on the rim ditches and beaches on the top of the stack were selected for radon flux measurements. Sampling at stations in the environment surrounding the New Wales facility was directed towards evaluating the ambient concentrations of radioactivity which might be affected by emissions from the New Wales facility.

RADIOASSAY OF PHOSPHOGYPSUM

Approximately two kilograms of phosphogypsum were collected and dried for 24 hours at 100°C. Approximately 600 grams of the dried phosphogypsum were then sealed in a 500 milliliter (ml) Marinelli beaker and allowed to equilibrate for three weeks to allow the ingrowth of radon-222 and its daughter products. The equilibrated samples were analyzed for radium-226 by high resolution gamma-ray spectroscopy. The procedure used to dry these samples will result in an over estimation of radium-226 concentration since the drying temperature will drive off moisture normally bound to the phosphogypsum crystals at environmental temperatures. This procedure was used so that the data collected in this evaluation could be compared to data collected in previous evaluations of other phosphogypsum stacks where the samples were prepared in a similar manner.

RADON FLUX MEASUREMENTS

Radon emanation was measured using the charcoal canister technique (Countess 1976). This procedure involves the deployment of charcoal collectors on the surface of the phosphogypsum stack or soil for approximately 24 hours. After deployment the charcoal is removed from the collector and sealed in a 500 ml Marinelli beaker and allowed to equilibrate for four hours to allow ingrowth of radon's daughter products. Radon content in the charcoal is then quantified by high resolution gamma spectroscopy. Radon flux from the surface of the sampled material in picocuries per square meter per second can then be estimated by adjusting for the surface area of the charcoal collector, the deployment time, and radioactive decay.

WORKING LEVEL MEASUREMENTS

Radon progeny measurements in working levels were made at selected sites using a Thompson & Nielsen Electronics Radon Sniffer working level meter (Thompson & Nielsen Electronics, 1987). This instrument operates by drawing air through a filter at a constant rate. Radon daughter products are collected on the filter and the alpha particle emissions from those daughter products are measured. Results of the measurement are reported in working levels.

AMBIENT RADON

Ambient radon in the vicinity of the New Wales facility was measured at eleven stations. These measurements were taken using Terradex Type F detectors deployed approximately 100 days during the first sampling episode and approximately 200 days during the second sampling episode (Gingrich, 1982). This monitoring technique involves the deployment of a plastic nuclear track detector mounted in a plastic cup with a filter permeable to radon placed over the open end. Radon from the atmosphere diffuses through the permeable filter and alpha particles from radon and its progeny penetrate the detector and cause radiation damage tracks that can be etched during analysis. The number of alpha tracks counted per unit area is proportional to the radon concentration in the ambient air. Results are reported in picocuries of radon-222 per liter of air.

RADIUM-226 IN SUSPENDED PARTICULATE MATTER

Radium-226 in ambient air was estimated from high volume air particulate filters previously collected at one of the sampling stations over the last 13 years. Radium-226 on the filters was measured using high resolution gamma-ray spectroscopy techniques. Concentrations of radium-226 in the sampled air were determined using historical records of the volume of air sampled. Results are reported in picocuries of radium-226 per cubic meter (pCi/m^3). Filters were selected for analysis based on the highest concentrations of particulate matter which were measured during a given year.

RESULTS

RADIUM-226

Table 1 summarizes the results of the analyses of phosphogypsum samples for radium-226. Results are summarized for all of the sites which have been sampled and then summarized for stations located at the top of the phosphogypsum stack and stations located on the side of the phosphogypsum stack.

Radium-226 concentrations in the phosphogypsum were relatively consistent, averaging 30.8 picocuries per gram (pCi/g) with a standard deviation of 5.4 pCi/g. Radium-226 concentrations measured in samples collected at the top of the stack did not differ substantially from concentrations measured in samples collected from the side of the stack.

It should be noted that the procedure used for drying the phosphogypsum samples will drive off moisture normally bound to the phosphogypsum crystals at ambient temperatures. Because of this, the radium-226 concentrations reported are higher (by as much as 25 per cent) than levels likely to be found in dry phosphogypsum in the environment.

RADON FLUX

Table 2 summarizes the results of the radon flux measurements. These measurements varied considerably ranging from a low of <0.1 pCi/m^2-sec on a rim ditch on the top of the stack to a high of 96.5 pCi/m^2-sec near a roadway on the top of the stack. Samples collected off the stack exhibited a mean radon flux rate of approximately five pCi/m^2-sec. Samples collected from the rim ditches and beaches on top of the stack exhibited mean radon flux rates less than one pCi/m^2-sec.

A substantial difference exists between the mean of the radon flux measurements collected near the roadways at the top of the stack and the mean of those collected from the side of the stack. Despite similar radium-226 concentrations

Table 1

RADIUM-226 IN PHOSPHOGYPSUM
(pCi/g)

	All Sites	Stack Top	Stack Side
Number of Samples	28	18	10
Mean	30.8	30.4	31.6
Standard Deviation	5.4	5.2	5.7
Range	22.8 - 45.1	23.1 - 40.4	22.8 - 45.1

Table 2

RADON FLUX
(pCi/m^2-sec)

	All Sites	Off Stack	Stack Top	Stack Side	Pond Beach	Stack Rim Ditch
No. of Samples	56	11	18	15	6	6
Mean	11.4	4.5	22.9	11.4	0.6	0.9
Standard Deviation	16.6	9.2	21.8	10.4	0.1	1.6
Range	<0.1-96.5	0.2-33.4	3.2-96.5	1.2-36.6	0.4-0.8	<0.1-4.5

as shown in Table 1, the mean radon flux level on the side of the stack is approximately half the mean level exhibited by stations near the roadways at the top of the stack. The lower radon flux levels exhibited on the stack side are probably due to the crusting which occurs on the stack side as well as the higher moisture content at these locations. Although the measurements varied considerably as shown in the sample ranges and standard deviations, the difference between the mean radon flux from the stack side and the stack top is considerable.

AMBIENT RADON CONCENTRATIONS

Ambient radon concentrations ranged from below the detection limit of 0.1 pCi/liter to 1.2 pCi/liter. The mean concentration was 0.4 pCi/liter with a standard deviation of 0.3 pCi/liter.

RADON PROGENY

Radon progeny measurements which were collected on and in the vicinity of the phosphogypsum stack are summarized in Table 3. These measurements varied considerably and ranged from zero to 0.0065 WL. The 0.0065 WL measurement was collected at a downwind location on the top of the phosphogypsum stack. As expected, the highest measurements obtained were those collected on the phosphogypsum stack. All of these levels are considerably below the indoor working level standard for the State of Florida. The mean of the ambient outdoor measurements collected off the stack were one percent of the indoor standard.

RADIUM-226 IN AMBIENT AIR

The results of the analyses of air particulate filters indicate radium-226 concentrations less than the minimum detectable activity measurable by high resolution gamma spectroscopy. However, based on the detection limits of the analytical procedure, it can be stated that the radium-226 concentrations associated with these samples are less than 0.1 picocuries of radium-226 per cubic meter of air sampled. These levels are considerably below the 2.0 pCi/m^3 MPC for radium-226 in air for the State of Florida.

RADIOLOGICAL IMPACT EVALUATION

ATMOSPHERIC DISPERSION MODEL

Airborne concentrations of radon in the vicinity of the phosphogypsum stack were determined using the ISCLT computerized atmospheric dispersion model (USEPA, 1986). This model is an EPA-approved methodology for estimating airborne concentrations of gases or suspended particulate matter and for determining deposition rates of settleable particulate matter at selected receptor points when emissions and meteorological data are known. Projected airborne concentrations and deposition rates produced by the ISCLT model can then be compared to standards and criteria to determine the significance of the emissions' impact.

RADIOACTIVITY EMISSIONS

The radon emission rates used for modeling purposes are the average emissions measured on the stack (Table 2). Since the expansion of the stack will be

Table 3

RADON PROGENY
(WL)

	All Sites	On Stack	Off Stack
Number of Samples	15	11	4
Mean	0.0014	0.002	0.0002
Standard Deviation	0.0020	0.0022	0.0004
Range	0 - 0.0065	0.0005 - 0.0065	0 - 0.0009
Indoor Standard	0.02		

phased, the modeling evaluation considered several phases to account for varying stack configurations and varying stack heights (see Table 4).

The radon emission rates used in the assessment are 22.9 pCi/m^2-sec from the stack top (roadways), 11.4 pCi/m^2-sec from the stack sides (crusted slopes), 0.6 pCi/m^2-sec from the pond beaches and 0.9 pCi/m^2-sec from the rim ditches. Radon is not emitted in significant quantities from the ponds on top of the stack (SENES, 1987). Table 4 summarizes the phosphogypsum field emission source characteristics during the phased expansion.

METEOROLOGY AND RECEPTOR POINTS

Meteorological input data used in the radiological evaluation were derived from observation at the Orlando International Airport for the years 1974-1978. Alternative evaluations using Tampa meteorological data produced similar modeling results. Receptor points for the radiological assessment were located at the nearest points of general public access near the New Wales facility and also at the location of the maximum exposed individual (MEI). The MEI is a hypothetical person located at the nearest residence to the facility for 24 hours per day during an entire year.

RADIUM-226 CONCENTRATION AND DEPOSITION ANALYSIS

The evaluation of maximum radium-226 concentrations and deposition rates was based on the results of the air quality particulate matter impact analysis for this project (IMC, 1988). Radium-226 concentrations and depositions were obtained by adjusting the particulate matter results by the concentration of radium-226 measured in the phosphogypsum (30.8 pCi/g).

DISPERSION MODELING RESULTS

Results of the atmospheric dispersion modeling are 'listed in Table 5. Also listed are the criteria which may be used for comparative purposes. Note that these criteria do not necessarily apply to ambient radioactivity concentrations in the vicinity of phosphogypsum stacks.

The maximum estimated contribution from the phosphogypsum stack to ambient radon levels is 0.000065 WL at a receptor located approximately 2000 meters south of the stack. This concentration is 0.3 percent of the State of Florida indoor radon standard. The maximum concentration at the location of the MEI is less than half this amount.

The maximum estimated radium-226 concentration in air is 0.00000012 pCi/m^3 which is less than one millionth of the 2 pCi/m^3 criterion. The maximum annual deposition rate for radium-226 is estimated to be 0.02 pCi/m^2. Typical undisturbed Florida soils contain 0.5 pCi of radium-226 per gram. At a density of 1.5 g/cm^3, the top six inches of such soils would contain 114,000 pCi of radium-226 per square meter. Deposition from the phosphogypsum stack at the maximum receptor for 1000 years would add less than 0.1 percent to the existing radium-226 in these soils.

Table 4

PHOSPHOGYPSUM FIELD
EMISSION SOURCE CHARACTERISTICS
USED FOR MODELING

	Stack Heights (ft)			Emission Area (acres)			
	Existing	Phase I	Phase II	Traveled Roadways	Crusted Slopes	Ponds Beaches	Rim Ditches
Case 1: Before Phase I startup	150	---	---	19	186	31	41
Case 2: At Phase I startup	200	0	---	38	255	34	83
Case 3: At Phase II startup	200	150	0	46	396	47	99
Case 4: At Phase II completion	200	200	200	49	470	19	95
Radon Emissions (pCi/m^2 - sec)				22.9	11.4	0.6	0.9

Table 5

ESTIMATED MAXIMUM CONTRIBUTIONS TO AMBIENT RADIOACTIVITY CONCENTRATIONS RESULTING FROM RADIOACTIVITY EMISSIONS IN THE VICINITY OF THE IMCF NEW WALES PHOSPHOGYPSUM STACK

	Radon Progeny in Air (Working Levels)			
	Maximum Offsite	MEI	Radium-226 in air (pCi/m^3)	Radium-226 Deposition (pCi/m^2/yr)
Case 1	0.000015	0.000009	0.00000006	.01
Case 2	0.000024	0.000013	0.00000008	.01
Case 3	0.000052	0.000024	0.00000011	.02
Case 4	0.000065	0.000027	0.00000012	.02
Criterion	0.02	0.02	2.0	--

CONCLUSIONS

The radium-226 measurements in phosphogypsum indicate a potential for the release of radioactive materials from the phosphogypsum stack via particulate suspension and distribution and radon emanation. However, ambient measurements of radon-222 in air and radium-226 in suspended particulate matter, and concentration and deposition estimates of the impacts of the proposed expansion are low. All measured levels and those estimatedby dispersionmodeling indicate that existing and future concentrations of these materials in the environment surrounding the New Wales facility are considerably below radiation protection criteria which could be applied to this area.

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Third International Symposium on Phosphogypsum

Phosphogypsum Management in Tunisia: Environmental Problems and Required Solutions

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ABSTRACT

Since the fifties, the phosphoric acid/phosphate fertilizer industry has developed significantly in a number of Tunisian cities. Two phosphogypsum piles are located in the area of the city of Sfax. The larger of these piles measures some 20 meters in height and covers an area of 80 hectares.

A groundwater assessment of this site revealed the existence of a highly polluted zone in the vicinity of the pile. High levels of phosphates, fluorine, mercury, and molybdenum were detected. Appropriate corrective measures are described.

INTRODUCTION

The development of Tunisia's phosphoric acid/phosphate fertilizer industry began in the fifties with the construction of a plant (SIAPE "A") at the coastal city of Sfax, second in population only to Tunis, the nation's capital. A second plant was added in the sixties.

Phosphoric acid is produced by dihydrate processing of natural phosphate, mined in the Gafsa region along Tunisia's southwest border with Algeria, using sulfuric acid. The main reaction occurs in a monotank producing a solid-phase product ($CaSO_4 . 2H_2O$) suspended in a solution of phosphoric acid (H_2PO_4), containing 27 to 28% P_2O_5 by weight (Chakchouk and Trabelsi, 1989). Secondary reaction products include calcium, iron, aluminium, and magnesium sulfates as well as significant quantities of hydrofluoric acid (HF).

The mixture is vacuum-filtered; the filtered solids are rinsed twice. The rince water is added to phosphogypsum, which is pumped to a storage basin. Once there, the liquid is decanted off to a spillway to the sea. In reality, there are two basins: one for active storage, the other for drying.

The stockpile to the south of Sfax covers some 80 hectares to an average of 20 meters with an average slope of 30°. The pile weights approximately 15 millions metric tons for a total in the Sfax area of 25 millions metric tons.

PROBLEMS ASSOCIATED WITH PHOSPHOGYPSUM

Leaching and environmental pollution are the two main problems encountered in storing phosphogypsum.

LEACHING

The production of each ton of phosphoric acid yields five tons of phosphogypsum, in the form of a fine sand composed of:

- calcium sulfate;
- free and syncrystallized phosphoric acid;
- various fluorine-containing acids;
- lead, zinc, mercury, copper, cadmium, and other metallic salts; and
- radioactive elements.

Chemical analysis of samples reveal the presence of significant quantities of various toxic compounds. The pH of Tunisian phosphogypsum is always very low (maximum: 2) because it is stored without neutralization. The concentrations of its main contaminants are given in Table I.

Comparison with standard values used in Quebec for classifying contaminated soils and materials (M.E.N.V.I.Q., 1988) shows that the phosphogypsum is:

- slightly contaminated by zinc and molybdenum, and
- highly contaminated by cadmium and mercury.

Furthermore, concentrations of phosphates and fluorine detected in the phosphogypsum are so high that it should be classified as a dangerous toxic waste.

Rain and storage water can seep through the phosphogypsum, carrying the contaminants to the soil and groundwater. The relatively good hydraulic conductivity of stored phosphogypsum (10^{-5} to 10^{-6} m/s) and the absence of a watertight barrier between the pile and the natural soil are powerful factors in the potential pollution of the surrounding environment.

CONTAMINATION BY STORAGE WATERS

Contamination by storage water can occur in two ways:

- Water passes through the stockpiled phosphogypsum forming a layer of polluted water that gradually seeps into the groundwater. Such a layer, some six meters in depth, was detected in the pile south of Sfax.

- Dumping this water directly into the sea from the storage basin without neutralization or treatment.

Chemical analysis of this water, shown in Table II, confirms a high rate of pollution. The presence of these contaminants in the phosphogypsum and storage water reveals the potential for environmental disaster in the following steps:

- seepage of rain and storage water through the phosphogypsum deposit;
- development of a very polluted water layer in the deposit;
- seepage of the polluted water into groundwater;
- migration of the contaminants throughout the groundwater and into seawater, a mere 1800 meters downstream from the deposit. The spread of pollution will dangerously affect the food chain (fish and the like).

This study was conducted to detect the presence of pollution, determine its extent, and characterize the main contaminants present in the groundwater in proximity to the phosphogypsum pile located 5 km to the south pf Sfax (SIAPE "A" pile).

EXPERIMENTAL

PIEZOMETER INSTALLATION

Sixteen two-meter deep holes were drilled with a hand auger. The holes were aligned in two orthogonal profiles (Fig. 1):

Profile 1: downstream of the mound towards the sea,
Profile 2: eastward from the mound.

A piezometer in PVC sealed at the top was inserted in each hole spaced from the pile as shown in Table III.

WATER SAMPLING

Two series of water samples were taken from each hole: the first on September 4, 1989; the second on November 13, 1989. Five-hundred-millimeter samples were taken according to the standards pertaining to the chosen analysis.

ANALYSES

Each sample was analyzed for the parameters listed below:

- pH.
- Phosphates by colorimetry.
- Fluorine by specific electrode.
- Metals by atomic absorption spectrometry and ionized argon plasma method.

RESULTS AND PRESENT STATEMENT OF POLLUTION

Investigations revealed that the soil under and around the pile is constituted essentially of silts and clayey sand with a hydraulic conductivity estimated between 10^{-5} and 10^{-6} m/s. The water table depth is about 1.5 m near the pile and 0.3 m near the coast.

RESULTS

Findings in this investigation can be categorized into four main areas of interest:

- pH: The pH was invariably lower than 2 in the pile's immediate vicinity. It increases to normal values (neutrality) 200 m in the downstream direction and 30 m laterally. Groundwater pH variations for both profiles are shown in Figure 2.

- Phosphates: Phosphate concentrations, shown in Figure 3, are extremely high in the pile's vicinity, attaining 16 280 mg/L in the main direction of flow. The level drops off with distance, stabilizing around 5 mg/L.

- Fluorine: Fluorine concentrations, shown in Figure 4, are similarly high near the mound and in the downstream direction. A maximum of 8795 mg/L was recorded, with an average rate in the 2 to 5 mg/L range.

- <u>Mercury and molybdenum</u>: Levels for these highly toxic metals are given in Figures 5 and 6, respectively.

The behavioural disparities noted for some contaminants can be explained by lithological differences when the holes were sunk. In fact, lithology varied from one site to the next, and vertically at the same site. The soil was composed of a mixture of sand and either silt, clay, calcite, or organic matter. Such variations impact on hydraulic conductivity and interaction with contaminants. All these factors affect contamination migration and contaminant chemical interactions with the soil.

PRESENT STATEMENT OF POLLUTION

Tables IV and V compare the pollution indicators used in this study to Tunisian (MET, 1988) and Quebec (MENVIQ, 1988) standards for profile 1 (downstream direction), and profile 2 (lateral direction), respectively.

This comparison reveals that, in terms of these indicators, the groundwater around the phosphogypsum pile is totally polluted. In fact, maximum values and minimum values detected widely exceed both Tunisian and Quebec standards (the most recent are used as a second reference).

The extent of pollution is shown in Table VI, in which a distinction between two levels of pollution were considered:

- high pollution when standards were exceeded by a minimum factor of 100 and
- moderate pollution when concentrations approximated standards.

This distinction was made to limit the area requiring corrective action due to economic and technical considerations.

The polluted water layer extended over an estimated 400 m seaward (downstream direction) and 100 m laterally.

CORRECTIVE MEASUREMENTS

The problems relating to the management and storage of phosphogypsum in Sfax identified by this study are:

- <u>Storage Water</u>

  - The use of polluted water for storage.
  - The increase in total contaminant content in the storage basin effluent.
  - The seepage into the stored phosphogypsum of water estimated equalling 40% of the total quantity of storage water.
  - The negative environmental impact of this effluent dumped untreated into the sea.

- Phosphogypsum

  - The leaching hazard posed by rain and storage waters seeping through phosphogypsum, thereby producing highly polluted water that will contaminate both ground and seawater.
  - The absence of hydrogeological barriers and leachate collection treatment systems.
  - The presence of very polluted water layers under and around existant piles. If left unchecked, this layer will spread, making correction economically and technically infeasible.

The solutions proposed herein are based on a few guiding principles.

- Phosphogypsum storage must be practiced so as to protect the environment in new sites;
- Existant storage piles must be controlled and closed.
- The polluted groundwater in the vicinity of existing piles must be contained and treated.

PHOSPHOGYPSUM STORAGE

New basins, protectedby hydrogeological barriers (liners) must be constructed for phosphogypsum storage. These basins must be equipped with appropriate leachate collection systems. The leachate would then be directed to basins used for treatment of polluted groundwater.

PROTECTION OF EXISTANT PILES

Since existing piles were not built with liners, there is an urgent need to cover them with the watertight material to be used on new storage basins.

POLLUTED WATER TREATMENT

The first step in this endeavour is building a slurry trench anchored in soil of low permeability. This lined trench should confine polluted water around the pile (Figure 7), inhibiting the migration of contaminants, stopping the spread of the highly polluted zone, and safeguarding the marine environment.

There are two viable paths for dealing with the polluted water:

- a treatment plant using chemical processes, or
- a natural evaporation process using basins or lagoons protected by watertight barriers. These lagoons can be located between the existing pile and the coast in the case of the SIAPE"A" plant (see Figure 7).

STORAGE WATERS

Storage waters can be recovered phosphogypsum basin effluent and be reused in the phosphoric plant as process water.

Storage water that seeps through the phosphogypsum will be collected by a drainage system and delivered to the water treatment system described above.

SUGGESTED TYPES OF HYDROGEOLOGICAL BARRIERS

Two different types of protection barriers can be used in the projected basins.

- One alternative is compacted clay with a hydraulic conductivity lower than 10^{-7} cm/s. To insure maximum safety, a double liner system with reinforced geomembrane is recommended. The minimal thickness of the barrier shall be 1 m. A drainage system will insure leachate removal.

- The second alternative involves using a liner comprised of a mixture of phosphogypsum, cement, and fly ash. This solution offers the double advantage of incorporating inexpensive industrial by-product used (phosphogypsum and fly ash) that are widely available in quantity. Research into mixtures of cement kiln dust, and class C fly ash, has shown that materials with very low hydraulic conductivity (10^{-11} m/s) and sufficient longevity can be obtained (Ballivy et al., 1989). Similar mixtures can be obtained using phosphogypsum, portland cement, and fly ash or silica fume.

This type of barrier offers several advantages:

- very low hydraulic conductivity;
- very good longevity and contaminant migration strength;
- sufficient strength and ductility for phosphogypsum storage and handling operations;
- possibility of use in cutoff wall construction; and
- relatively low cost.

CONCLUSION

The major findings of this study of one of the phosphogypsum piles in Sfax (Tunisia) are summarized below.

- Present phosphogypsum procedures are not in accordance with environmental standards.
- Phosphogypsum leaching has severely polluted the groundwater up to several hundred meters around the pile.
- There is a critical need to replace present practices of Tunisian phosphogypsum management with technology that safeguards the environment.
- There is a concommitant urgent need to remedy the existing situation that has resulted from three decades of mismanagement.

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Table I. Average concentrations of contaminants in Tunisian phosphogypsum

Indicator of contamination	Concentration (mg/kg)	Limit value Quebec standard (mg/kg)
Phosphates (P_2O_5)	31 000	*
Fluorine	40 000	*
Zn^{2+}	315	100
Cd^{2+}	39.8	1.5
Hg^{2+}	14.5	0.2
Ni^{1+}	15.4	50
Fe^{2+}	58.4	*
Cu^{2+}	5.9	50
Mo^{2+}	5	2
Co^{2+}	7.6	15

* not available

Table II. Chemical composition of water used for phosphogypsum storage (at the landfill entry)

Chemical Compound	Concentration (mg/L)
F	5539
Cl	1520
SO_4	5385
P_2O_5	4015
Ca	1654
SiO_2	2018
Na	2556
K	62
Mg	182
Fe	12.8
Al	0.414
Zn	3.952
Hg	0.61
Cd	0.62
Ti	0.42
Co	0.18
Sr	28
Pb	0.18
Cr	2.73
Cu	0.082
Suspension	19 503.0
pH	1.8

Table III. Location of piezometers

a) Profile 1 (Downstream direction)

Piezometer number	1	2	3	4	5	6	7	8	9
Distance from pile (m)	0	25	150	200	300	400	500	750	1000

b) Profile 2 (Lateral direction)

Piezometer number	1	2	3	4	5	6	7
Distance from pile (m)	30	55	75	100	150	200	300

Table IV. Groundwater pollution statement in downstream direction

Indicator of contamination	Maximal value (mg/L)	Minimal value (mg/L)	Limit value Tunisian standards (mg/L)	Limit value Québec standards (mg/L)	Ground-water quality
pH	7.3	1.2	5.9	*	Polluted
Fluorine	8795	6.65	0.1	0.3	Polluted
Phosphates (P_2O_5)	16280	4.28	0.23	0.05	Polluted
Mercury	0.60	0.1	0.001	0.0001	Polluted
Molybdenum	0.193	0.05	*	0.0005	Polluted

* not available

Table V. Groundwater pollution statement in lateral direction

Indicator of contamination	Maximal value (mg/L)	Minimal value (mg/L)	Limit value Tunisian standards (mg/L)	Limit value Québec standards (mg/L)	Groundwater quality
pH	7.54	6.55	5.9	*	Polluted
Fluorine	47.56	2.87	0.1	0.3	Polluted
Phosphates (P_2O_5)	34.57	6.58	0.23	0.05	Polluted
Mercury	0.139	0.100	0.001	0.0001	Polluted
Molybdenum	0.327	0.073	*	0.0005	Polluted

* not available

Table VI. Pollution extension around phosphogypsum pile

Indicator of contamination	Extension of polluted zone from pile			
	Downstream direction		Lateral direction	
	High level (m)	Moderate level (m)	High level (m)	Moderate level (m)
pH	100	—	30	—
Phosphates	400	1000	80	300
Fluorine	100	1000	80	300
Mercury	100	1000	100	300
Molybdenum	400	1000	100	300

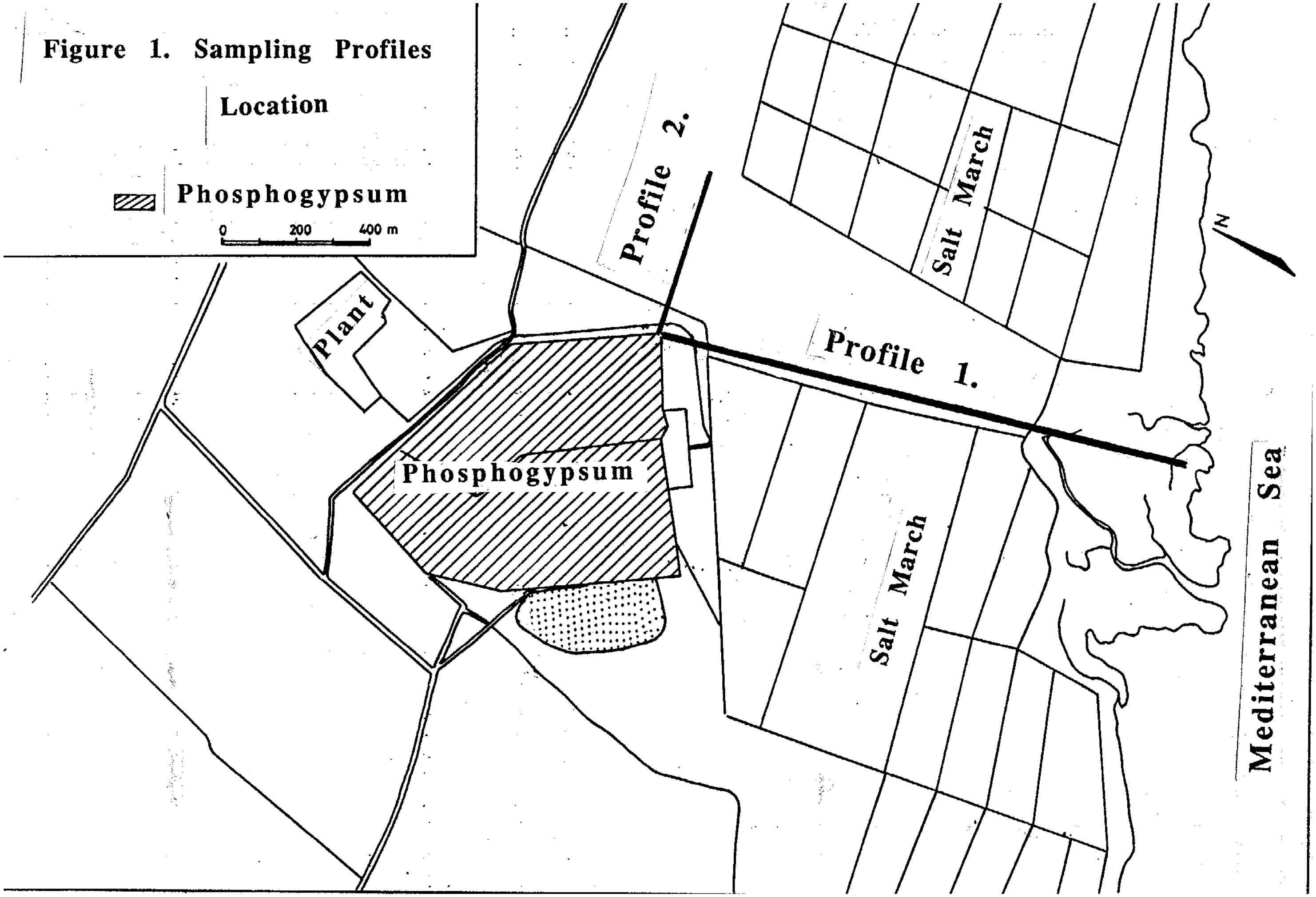
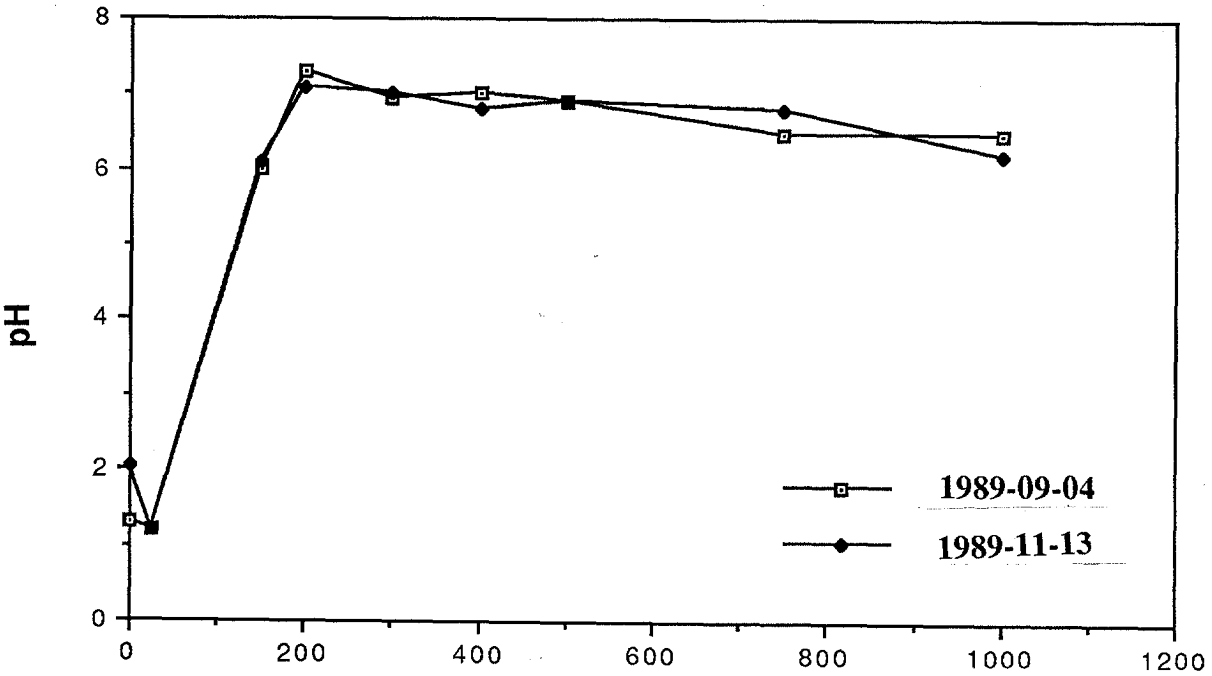
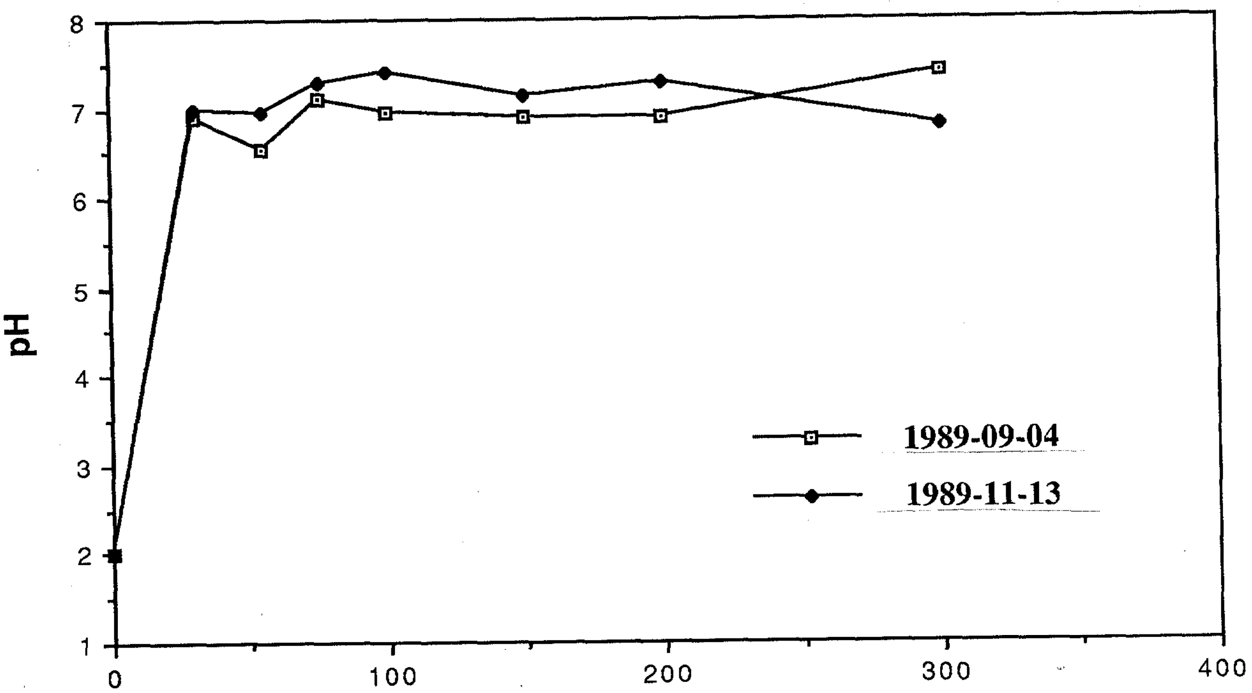


Figure 1. Sampling Profiles Location

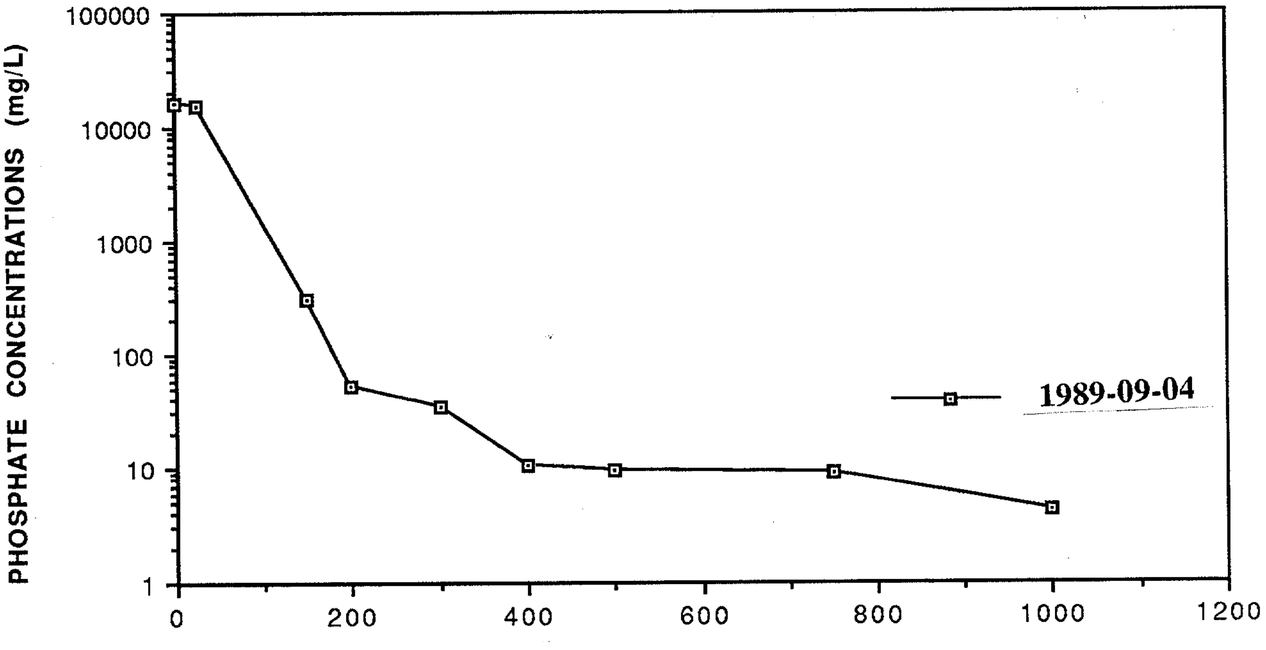


DISTANCE FROM LANDFILL (m)
a- DOWN STREAM DIRECTION

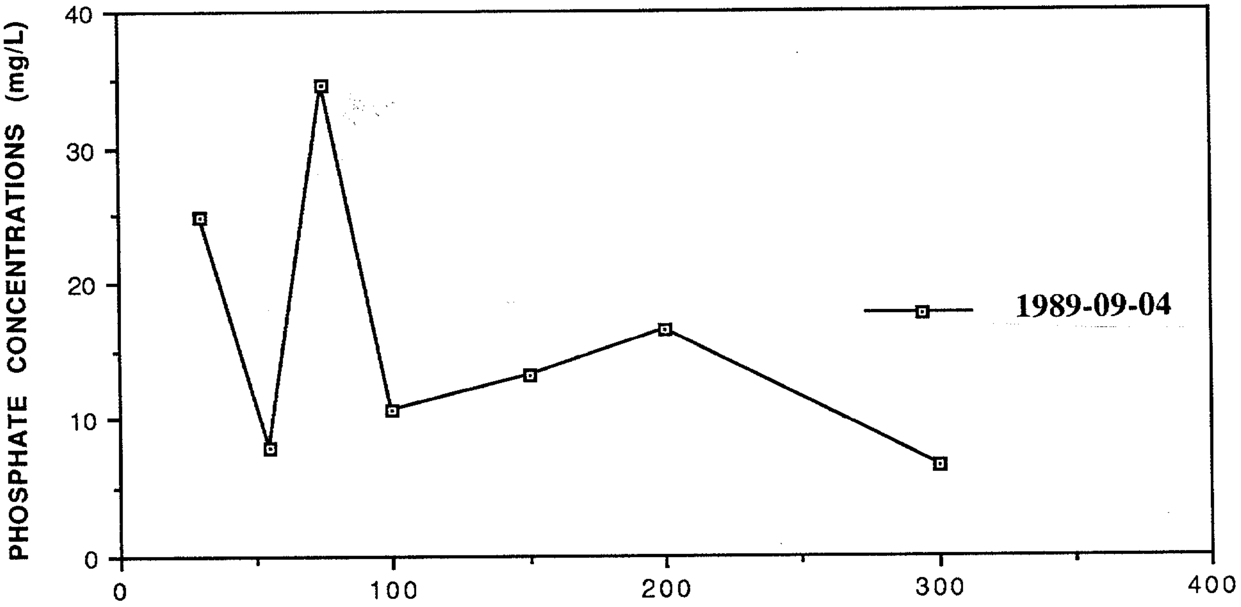


DISTANCE FROM LANDFILL
b-LATERAL DIRECTION

Figure 2. GROUND WATER pH AROUND PHOSPHOGYPSUM PILE

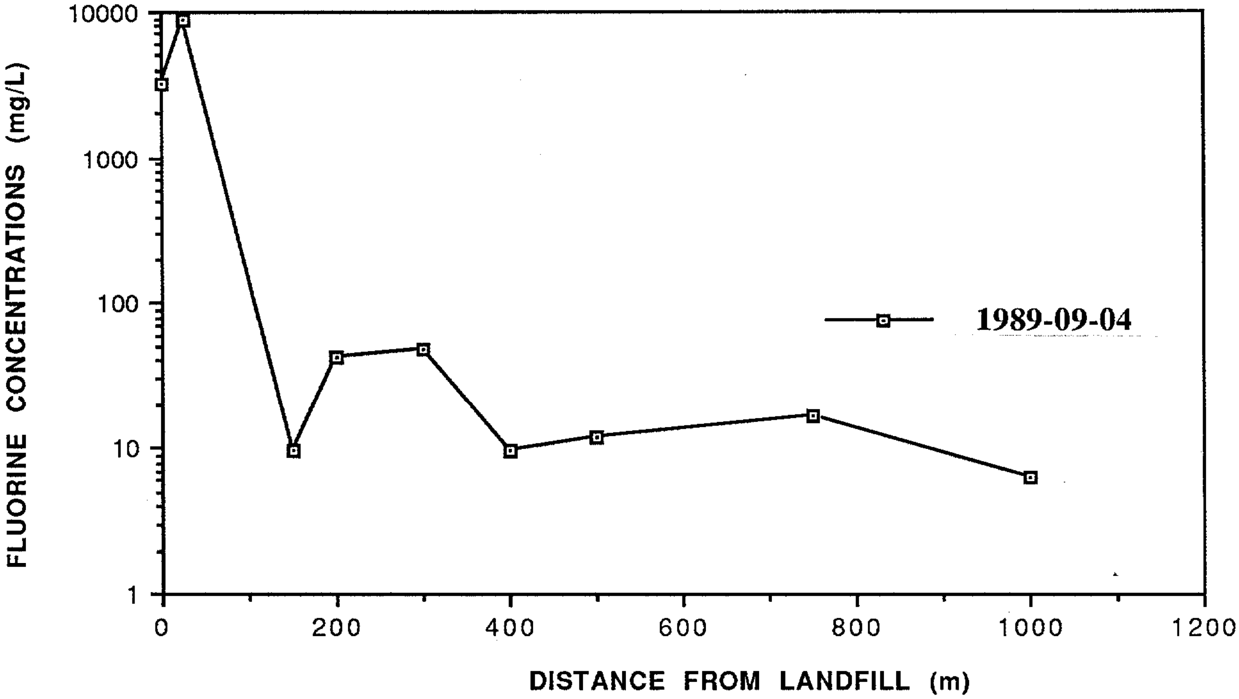


a- DOWN STREAM DIRECTION

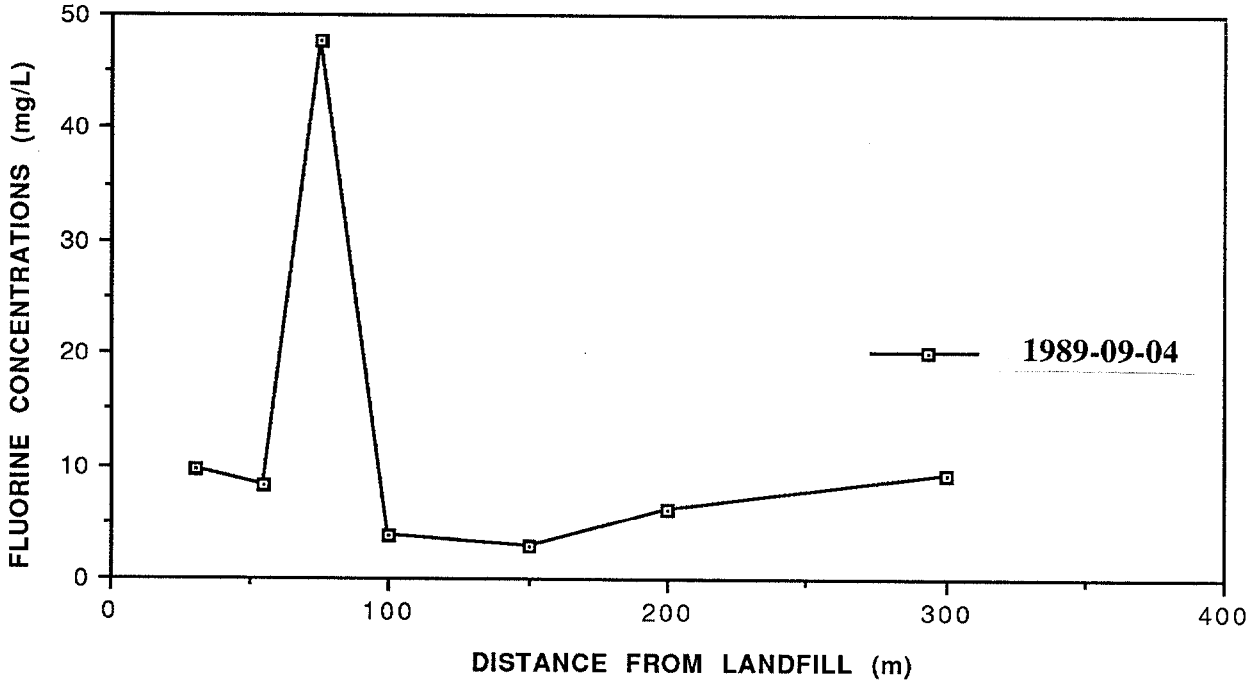


b- LATERAL DIRECTION

Figure 3. GROUND WATER PHOSPHATES CONCENTRATIONS AROUND PHOSPHOGYPSUM PILE

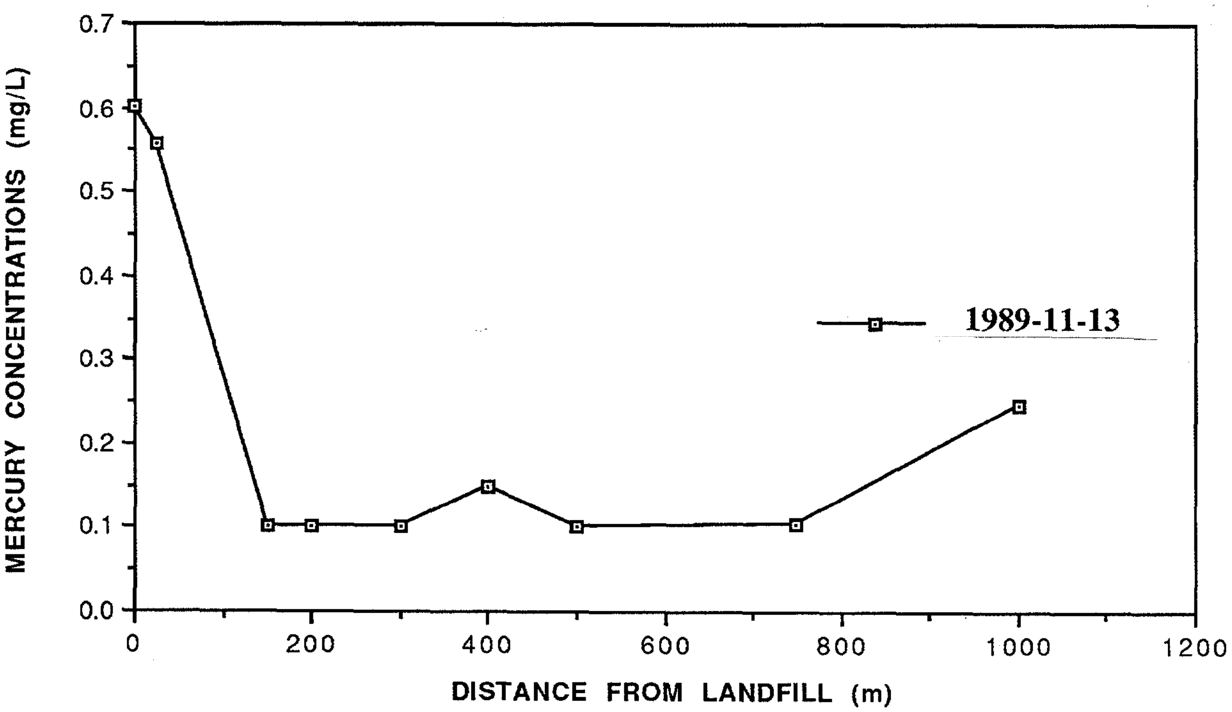


a- DOWN STREAM DIRECTION

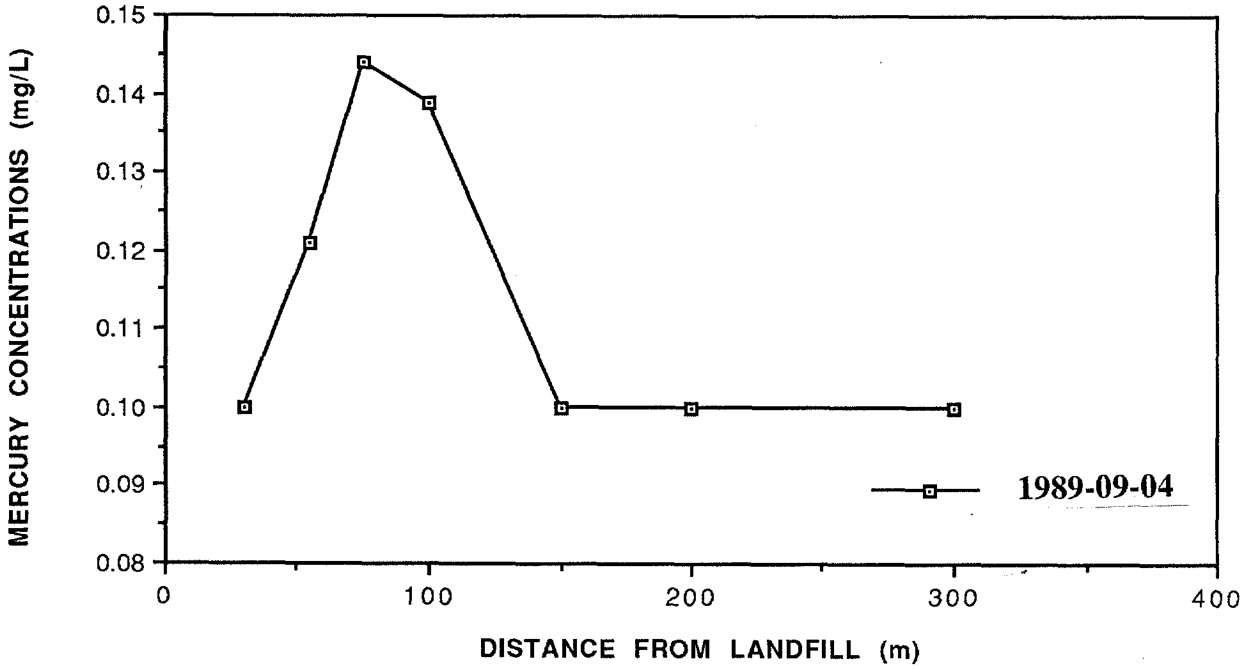


b- LATERAL DIRECTION

Figure 4. GROUND WATER FLUORINE CONCENTRATIONS AROUND PHOSPHOGYPSUM PILE

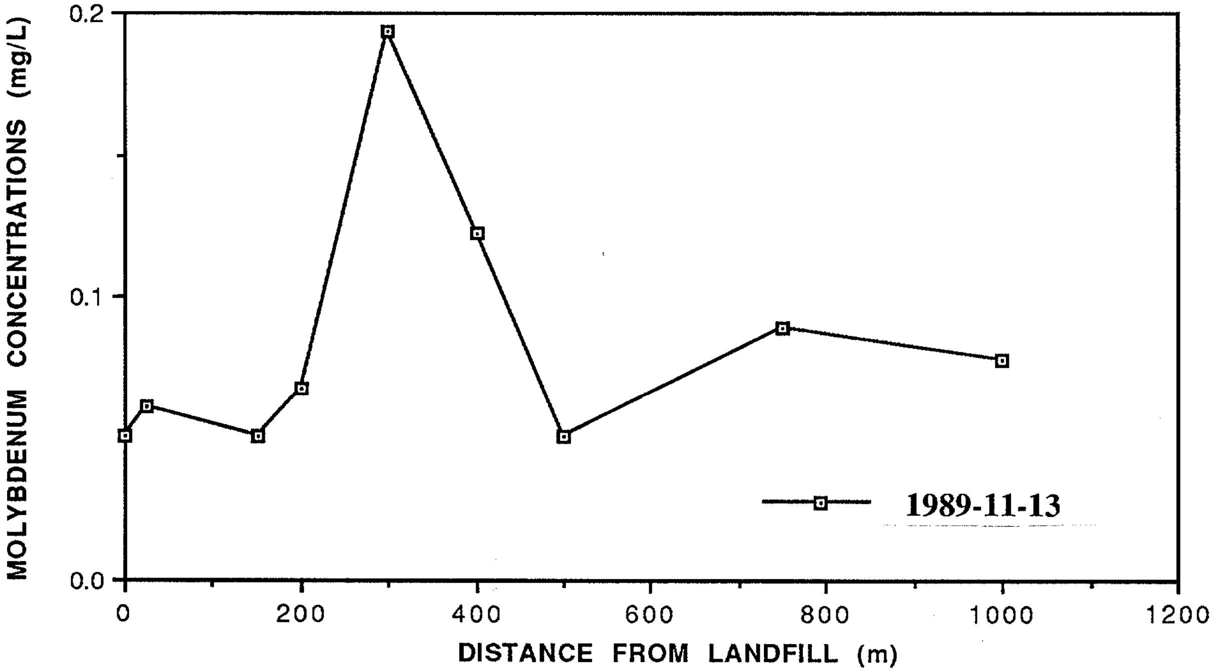


a- DOWN STREAM DIRECTION

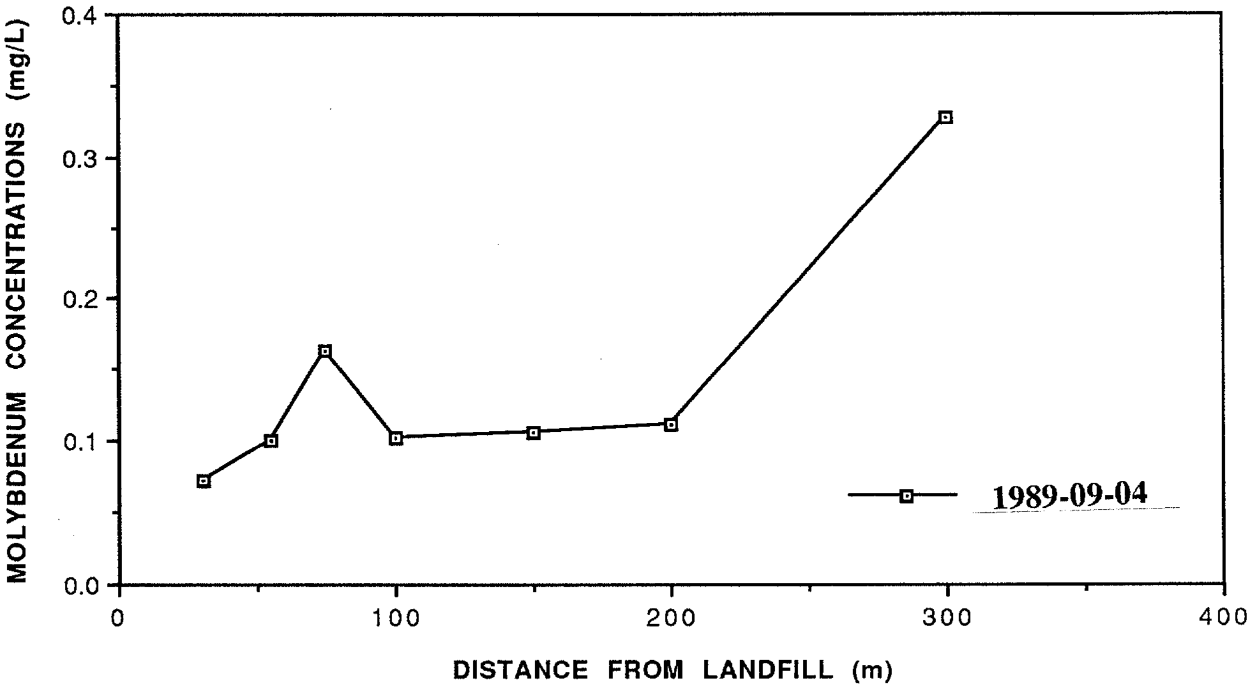


b- LATERAL DIRECTION

Figure 5. GROUND WATER MERCURY CONCENTRATIONS AROUND PHOSPHOGYPSUM PILE



a- DOWN STREAM DIRECTION



b- LATERAL DIRECTION

Figure 6. GROUND WATER MOLYBDENUM CONCENTRATIONS AROUND PHOSPHOGYPSUM PILE

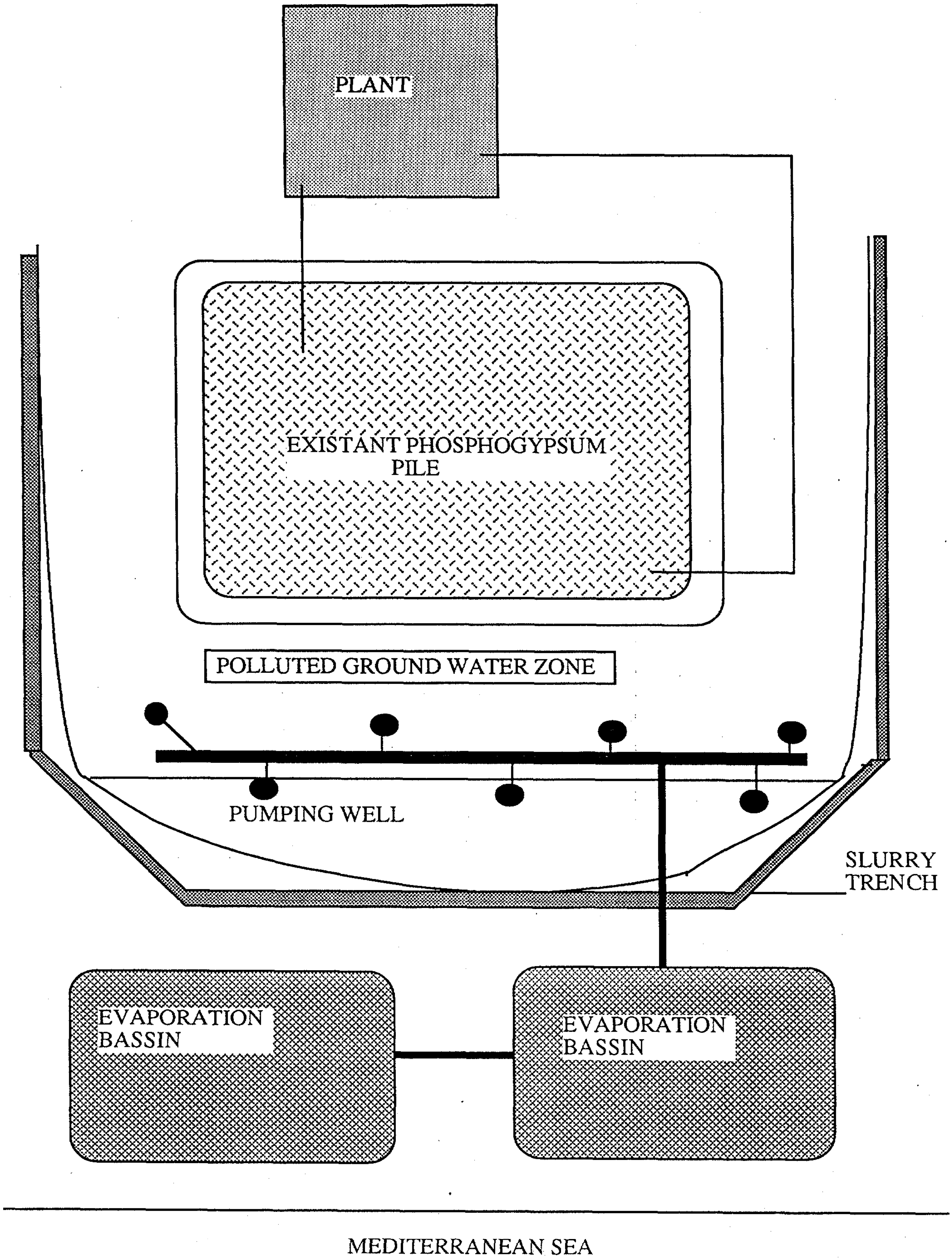


Figure 7. CORRECTIVE MEASURES FOR EXISTANT PILE

PHOSPHOGYPSUM STACK CLOSURE

BY

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GENERAL

INTRODUCTION

GYPSUM STACK OPERATION

GYPSUM STACK CONSTRUCTION AND TOPOGRAPHY

GEOLOGIC AND HYDROGEOLOGIC SETTING

HYDROLOGY AND SURFACE WATER QUALITY

STACK CLOSURE PLAN

ENGINEERING ASSESSMENT

PROPOSED MONITORING:

- Field Exploration
- Laboratory Analyses & Characterizations
- Surface Water Runoff Analyses
- Surface Erosion Analysis
- Evaluation of Gypsum Stack Water Drainage
- Toe Drain Evaluation
- Top Cap Membrane Selection
- Grading Plan
- Final Surface Cover
- Stormwater Management
- Leachate Control

PERMITTING

- Time-Table For Implementation

CONSTRUCTION

- Grading
- Plastic Membrane Cap
- Shoreline Restoration

ABSTRACT

Decommissioning and closing a gypsum stack requires knowledge of the geology and hydrogeology under the stack and the surrounding area. Geotechnical investigations are made of the stack to determine water levels, permeability and hydraulic conductivity, Infiltration of surface run-off into the stack must be known to determine the amount and duration of leachate from the stack.

The closure design should consider the following:

Groundwater impacts
Leachate control
Control of infiltration
Stormwater management
Visual management

Data are presented in this paper in the form of a case history for closure of Gardinier's gypsum stack. This stack's location, age, height and existing flatter than normal side slopes, make this a unique case. It appears, however, that each stack closure will be unique in many aspects.

INTRODUCTION

Gardinier's existing gypsum stack is located approximately seven miles south of Tampa, Florida adjacent to Hillsborough Bay, near the mouth of the Alafia River. See Figure 1.1, Site Location Map.

The stack construction was started in the early 1950's by constructing containment dikes from gypsum placed in the same area prior to this time.

In 1984, Gardinier received permits from Hillsborough County and the State of Florida to construct a new gypsum disposal field. One of the stipulations in each of the permits was to decommission the existing stack and prepare a closure plan acceptable to the respective environmental regulatory agencies.

The major features of the closure plan include the following:

- Transfer ponded process water from the top of the stack to process water storage ponds,
- Construction of a new buried toe drain on the south, west and north sides to collect leachate.

- Grading the top of the stack to provide positive drainage; installing a 40 mil HDPE top cover; covering the plastic cover with 18 inches of soil and grassing.
- Grading side slope roads into drainage channels sloped to flow to stormwater retention ponds; covering the graded channels with clayey sands and grassing.
- Construction of a surface water management system to collect rainfall and to meter runoff from retention ponds.
- Placing a cover of top soil and grassing all areas of side slopes which are bare or with insufficient grass cover.

The work was planned to be started in May, 1990 and be completed in mid 1991. The total cost will be approximately 5.5 million dollars.

The data contained in this paper are extracted from "Area Information and Closure Plan, Existing Gypsum Storage Area" prepared by Ardaman & Associates, Inc., 1989. This firm conducted the field exploration, analyses and prepared the plan documents. They have also prepared the contract drawings and specifications for the closure construction work.

GYPSUM STACK OPERATION

Gypsum is produced as a by-product in the manufacture of phosphoric acid. Gardinier employs the dihydrate process which uses concentrated sulfuric acid (H_2SO_4) to dissolve fluorapatite ($Ca_{10}(PO_4)_6F_2$) contained in phosphate rock. Through this process, phosphoric acid (H_3PO_4) is produced along with by-products of fluosilicic acid (H_2SiF_6) and phosphogypsum ($CaSO_4$-$2H_2O$). Gypsum is removed from the mixture by filtration and is discharged to the disposal stack as a slurry mixture: usually about 30 percent gypsum crystals and seventy percent acidic process water.

The gypsum slurry is pumped to the top of the stack and discharged into perimeter deposition ponds. The process water is decanted into a center storage pond and then removed from the stack via a syphon.

Recently the Gardinier stack was rising at a rate of slightly less than 20 feet per year. The total dry gypsum produced at full plant capacity is approximately 3,600,000 tons per year.

GYPSUM STACK CONSTRUCTION AND TOPOGRAPHY

The base of the stack occupies approximately 340 acres with an operational top area of approximately 100 acres. The stack height is 225 feet (NGVD) at the south (slurry discharge) end and 215 feet (NGVD) at the north end.

The side slopes below elevation 115 feet (NGVD) are 4.0 horizontal to 1.0 vertical (4:1). Above elevation 120 feet, the slopes range from 3.0 to 3.2:1, Typically, fresh gypsum placed at the exterior of the outer dike was sloped at 2:1 but consolidation and settlement flatten the slope as additional lifts of fresh gypsum were placed on the dikes.

The side slopes of the stack were covered with six inches of top soil and grassed. Underdrains are located beneath the slope surface to intercept leachate water and reduce seepage breakouts at the side slope surface.

The stack is surrounded by a buried toe drain which consists of two (2) 18 inch diameter perforated pipes. The pipes are embedded in a filter sand drain, The pipe gradient is approximately 1 foot vertical per 1,000 feet horizontal (1:1000) with the average pipe invert elevation at -0.16 (NGVD).

GEOLOGIC AND HYDROGEOLOGIC SETTING

The geology and hydrogeology summary is from a groundwater monitoring plan report (Ardaman & Associates, 1983). The stack lies within the Pamlico Terrace which is a Quarternary Age erosional surface about two miles wide paralleling the east shore of Hillsborough Bay. The terrace terminates inland at a low topographic bluff marking the transition from this terrace to an older slightly higher one to the east. Geologic sections under the stack are shown on Figures 1.2 and 1.3. The Pleistocene deposits and Hawthorne formation are as indicated by test borings performed by Woodward-Thorfinnson & Associates (reports October, 1974 and September, 1976).

GEOLOGY

The site is underlaid by approximately 8,000 feet of sedimentary rock. The upper 700 feet consists of, from youngest to oldest, undifferentiated Pleistocene deposits, the Hawthorne formation of Miocene Age, the Tampa limestone, also of Miocene Age, Suwannee limestone of Oligocene Age,

Ocala group limestone and Avon Park limestone, both of Eocene Age. This stratigraphy, as well as that of the entire peninsula of Florida, is a typical sedimentary domain resulting from sea level transgressions and regressions. The strata were deposited in horizontal layers with little subsequent distortions or warping.

The base of the Avon Park limestone is considered the base of the Florida Aquifer; however, at this site the Avon Park and Ocala group limestone are saline. The Suwannee limestone and Tampa formation are, therefore, the deepest formations of interest as they form the top section of the Floridan aquifer and have the least mineralized waters within it. The Suwannee limestone, described by (Yon and Hendry, 1972) is a hard crystalline limestone with a pale orange color. According to the report "Evaluation of Gypsum Field Stability", Volume 1, by (Woodward-Clyde Consultants, October, 1974) the Suwannee formation at the site is between 230 and 280 feet thick, The Tampa formation below the site consists of creamy white, gray and tan, fairly hard, porous to dense, sandy limestone which is fossiliferous and silicified in part. Based on various well logs contained in the Woodward-Clyde report, and at least two holes documented by USGS with lithologic logs, the Tampa formation below the site is estimated to be about 60 to 67 feet thick.

The Tampa formation is overlain by the Hawthorne formation of Miocene Age which exhibits great variation in composition and properties. Included are gray, greenish-gray, or blue-grey, sandy phosphatic clays, sandy limestones, sands, silts and shells. The thickness varies from a few feet to about 60 feet.

The surficial soils form a part of the Pamlico sands and consist of an undifferentiated Pleistocene (Quarternary) deposit of organics, sands, shells, clays and calcareous clays. The thickness ranges from several feet to about 30 feet.

The basic geologic deposits which underlie the site are summarized as follows:

DEPTH - FEET		
FROM	TO	GEOLOGIC DESCRIPTION
0	10 to 30	Pleistocene Deposits
10 to 30	15 to 90	Hawthorne Formation
15 to 90	75 to 157	Tampa Limestone
75 to 157	305 to 437	Suwannee Limestone
305 to 437	545 to 680	Ocala Group Limestone
545 to 600	≃ 1340	Avon Park Limestone

HYDROGEOLOGY

The groundwater regime underlying the site consists of three aquifer systems: the surficial, the intermediate and the Floridan aquifer. The surficial aquifer is unconfined and consists of the Pleistocene deposits which are predominantly fine sands with some clays. Based on the (Woodward-Clyde reports, September 23, 1976 and March 28, 1977) the average permeability is estimated at 0.7 to 2.2 feet per day. This layer is sufficiently porous and permeable to permit infiltration and storage of groundwater. Recharge to this surficial water table aquifer is by local rainfall. Discharge is mainly by evapotranspiration and flow to the west toward Hillsborough Bay. The gradient is locally altered by the man-made gypsum stack, ditches, cooling ponds and other seepage sources. The depth to the water table is quite variable depending mostly on local rainfall but also dependent on water levels in ditches, Numerous test borings within the site indicate the water table to be at an average depth of about five feet below natural ground surface. During the wet season, the water table may rise close to the ground surface. Generally, water from this aquifer is not available in desirable quality or quantity for potable supply and is, therefore, not a source of water supply in the area (Menke, et al., 1961).

The intermediate aquifer system is found in the sand and limestone beds of the Hawthorne formation and in isolated cases can produce significant quantities of highly mineralized water, According to Woodward-Clyde Consultants (report of March 28, 1987) the coefficient of permeability in the limestone layers of the Hawthorne formation ranges from 0.25 to 0.9 feet per day. The intermediate aquifer is not a major water producing aquifer on this site because of its variable thickness and area combined with brackish water in wells near the Tampa Bay and Alafia River.

The upper Floridan aquifer is beneath the Hawthorne formation and is separated from it by a stiff greenish clay near the top of the Tampa formation. At this site the clay layer is typically 10 to 20 feet thick; however, the layer is absent in more than half of the Gardinier well logs. The Floridan aquifer which underlies the site includes the Avon Park limestone, Ocala group limestone, Suwannee limestone and Tampa formation limestone. Numerous wells on the Gardinier property have been drilled 800 to 1200 feet into limestone and yield highly mineralized water most of which comes from the Avon Park limestone. Various field permeability tests, indicate a wide variation field within the Floridan aquifer ranging from 0.05 to 22 feet per day. (Stewart, 1980) places this site in an area of very low recharge to the Floridan aquifer. It is estimated to be less than two inches per year.

The potentiometric surface of the Floridan aquifer in May, 1987, for this region (Lewelling, 1987) is shown on Figure 1.4. For this site the elevation of the potentiometric surface was approximately +3.0 feet (NGVD). Generally, water within the aquifer flows west toward Hillsborough Bay, but it is also affected by cones of depression. Based on an average head difference between the surficial and Floridan aquifer of 12 feet and a specific flow through the confining layer at 5.0 x 10^{-4} GPD/FT^{3}. (West Coast Regional Water Supply Authority, 1978), this corresponds to a vertical permeability for a 20 foot thick confining layer of approximately 0.001 feet per day.

GROUNDWATER QUALITY

Groundwater data west of U. S. Highway 41, from the Groundwater Monitoring Plan (Ardaman, 1983) and subsequent monitoring, indicate G-III and G-IV aquifer classifications. The Floridan aquifer and intermediate systems are Class G-IV because the total dissolved solids (TDS) in the aquifer exceed 10,000 mg/l and the aquifer is confined. The aquifer becomes increasingly non-potable with depth. Along Hillsborough Bay, the deeper portions of the aquifer contain dissolved solids content similar to sea water. Thus, deep wells in this area yield brackish to saline water.

The surficial aquifer system west of U. S. Highway 41 is Class G-III. The site is surrounded on three sides by brackish water. The land surface for natural ground beneath the gypsum stack ranges from 0 to 5 feet (NGVD). High tides are +2 feet (NGVD) approximately. The sands are relatively permeable. therefore, allowing brackish surface water to freely enter the groundwater system. The aquifer is unconfined.

STACK CLOSURE PLAN

PHASED CLOSURE PLAN:

Decommissioning of the existing gypsum stack has coincided with start-up of the new gypsum disposal field, In general, the Closure Plan has the following five major tasks:

1. Fill top cavity and initial dewatering.
2. Leachate control.
3. Restore shoreline grades and vegetation adjacent to Hillsborough Bay.
4. Infiltration reduction.
5. Stormwater management.

FILL TOP CAVITY AND INITIAL DEWATERING:

A water clarification pond existed on top of the stack with a total volume of approximately 90 million gallons. Gypsum was deposited into shallow perimeter deposition ponds arranged around the perimeter of the top surface. The inner and outer dikes which defined these ponds extended 8 to 10 feet above the center area of the stack. The depth of the water pond was 28 to 30 feet below the elevation of the outer dike.

The gypsum slurry lines were rerouted to discharge directly into the center area of the stack thus filling the center area with gypsum, The slurry lines were placed along the north-south centerline of the stack top and raised above the surface so as to create a ridge of material along this same line.

The perimeter deposition ponds were also filled by direct discharge from one of the gypsum slurry lines.

Dewatering ditches were excavated along the inner dikes so that dewatering was continuous as the center cavity was filled. The water was drained to a sump at the north end of the stack and syphoned off to be recycled as process water.

After filling the cavity, the dewatering ditches were maintained for the next two months to lower the level approximately 8 feet below the top surface.

When the top surface had dewatered sufficiently to support heavy equipment, grading commenced to achieve the configurations shown on Figure 1.5. The typical cross-sections of the graded top surface and the perimeter berm are shown on Figures 1.6 and 1.7. The top drainage swales slope from south to north about 0.4 percent.

The perimeter berm around the top of the stack will retain stormwater runoff on the top, thus allowing it to drain to the lower north end for a controlled discharge from two overflow spillways to the retention pond at the bottom of the stack.

LEACHATE CONTROL:

Water presently entrained in the stack will continue to drain for several years after decommissioning; see Figure 1.8, "Height of Gypsum Stack Phreatic Surface Vs. Time". Leachate collected is conveyed to a reservoir of operating process water or is neutralized and released through a plant outfall.

Leachate drainage from the Gardinier stack has been collected in a buried "toe-drain". The original drain had collapsed in several locations and was suspected of being bypassed in areas where it was shallow. The drain on the east side of the stack was intact and operating acceptably.

In 1987, a decision was made to replace the drain on the north, west and south sides with a new design. The new drain shown in Figure 1.9, consists of two 18-inch diameter perforated pipes with an outer sleeve of a knitted polyester fabric. The pipes are fabricated from high density polyethylene (HDPE). The drain pipes are embedded in a sand filter bed. The pipe invert elevation varies from a high of +0.17 feet (NGVD) to -4.5 feet (NGVD) at the discharge to the leachate collection sump at the northeast corner of the stack.

Figures 1.10 and 1.11, "Piezometer Installation Details", show that the measured water level in piezometers located between Hillsborough Bay and the toe-drain are higher than the water levels in the toe-drain. These observations indicate that the groundwater flows in these zones are toward the drain. Thus, one can conclude that the toe-drain provides effective control of leachate drainage.

RESTORE SHORELINE GRADES AND VEGETATION:

The west toe of the gypsum stack is adjacent to the shore of Hillsborough Bay. During the 1930's before the formal stack construction was begun, gypsum was discharged to this same general area with an overflow to the Bay. The gypsum in the water has long since been eroded, leaving a 4-foot escarpment of gypsum at the water's edge as the only residual trace. The escarpment ran along the shore for approximately 1300 feet. Restoration of this shoreline is an integral part of the stack closure.

Restoration included grading the gypsum escarpment to a uniform slope of 7 feet (horizontal) to 1 foot (vertical), 7:1. The graded surface was covered with top soil and four varieties of salt water grasses were planted at appropriate elevations above sea level. Natural propagation of red mangroves started soon after the grading was completed. It is anticipated that the entire shore will re-vegetate with mangroves.

INFILTRATION REDUCTION:

Leachate drainage, both quantity and rate of seepage, from the gypsum stack have a direct impact on the continued stack maintenance. It is Gardinier's obligation to collect and dispose of the leachate, either by pumping to process water storage ponds or by a neutralization treatment and discharge through a plant outfall.

Analyses were performed using the stack geometry shown earlier in this section, Figure 1.5. Based on measured field and laboratory test data from this stack and other phosphogypsum projects, the following engineering properties of phosphogypsum were selected for seepage and drainage:

Effective Porosity, N_e: 0.05 to 0.33

Coefficient of Horizontal Permeability, K^h: 5 x 10 -5 to 3 x 10 -4 cm/sec.

Coefficient of Vertial Permeability, K^v: 1.3 X 10 -6 cm/sec

Based on a gypsum volume of approximately 41,000 acre-feet and using the measured effective porosities with depth, the amount of water that will drain from the closed stack is estimated to be 1.5 billion gallons.

A parametric study was conducted to determine the effects of various top cap thicknesses and permeabilities due to rainfall. Water balance analyses were performed using the "Hydrologic Evaluation of Landfill Performance (HELP) computer model developed by the U.S. Army Engineer Waterways Experiment Station in Vicksburg, Mississippi. The percolation rates were unacceptable; therefore, an impermeable top cap was proposed. Based on other applications at the Gardinier Facility, a 40-mil high density polyethelene (HDPE) membrane was selected. The plastic is covered by 18 inches of local fill and top soil to protect it from ultraviolet exposure and promote grass growth.

The side slopes of the stack had been grassed under a previous Consent Order. The grass grows well so that an annual evapotranspiration rate of 30 to 40 inches per year is expected.

Slope infiltration is being determined by a field experiment, see Figure 1.12, Slope Infiltration Apparatus. This experiment will continue for two years and will monitor infiltration into the test area. If significant infiltration is documented, other alternatives will be evaluated.

The predicted quantity and rate of drainage from the stack is presented in Figure 1.13. The data shown are based on an impermeable top cap and an upper limit of allowable infiltration through the side slopes of 5 inches per year.

STORMWATER MANAGEMENT:

The flow of stormwater off the stack after closure, is shown on Figure 1.14. This area of the plan received the most attention from the regulatory agencies. A principal challenge was the design of retention ponds to receive water from the four sides of the stack. Sub-basin areas are shown on Figure 1.14 and are listed in Table A.

Runoff from the south slope sheet flows to a littoral pond located at the southwest corner of the Gardinier site.

Runoff from the top, north slope and areas of the east and west side slopes above elevation 50 feet (NGVD) flow directly to the north retention pond which is sized to retain and treat the first 1/2 inch of rainfall runoff from the 265 acres of the watershed area. Connected to the north pond is a long narrow pond constructed along the east side of the stack, The total capacity of the north and east ponds is 50 acre-feet, Runoff from the upper portions of the east and west slopes is routed along benched flow channels which also serve as maintenance roads. The channels have a slight gradient (0.5 percent). The channels are lined with soil to promote grass growth. Drop inlets and outlet pipes convey stormwater from the channels to the north retention pond. Energy dissipators are located at the pipe discharges.

Stormwater runoff from the lower 50 feet of the west slope sheet flows to a smaller retention pond located along the west toe road, The pond discharges to Hillsborough Bay via an underdrain system.

The north retention pond stores 4 feet of water above the seasonal high water level. An outlet structure discharges to Archie Creek, which, in turn, flows to Hillsborough Bay. Discharge from the pond is through an overflow spillway at elevation 4 feet (NGVD) and through an underdrain system. It is not maintained as a wet pond. A section through the north retention pond is shown in Figure 1.15.

PERMITTING

During the final stages of obtaining approval for the new gypsum field design, Gardinier, Inc. was informed that a separate permit would be required. The basis for this closure permit would be the solid waste disposal regulations.

The initial closure plan was submitted in December, 1988. Discussions and review meetings were held jointly with Florida Department Environmental Regulation (FDER) and Hillsborough County Environmental Protection Commission, (HCEPC).

Since this was to be the first gypsum stack closure in Florida, all parties moved cautiously through the review process. Existing solid waste regulations did not cover all the situations nor did those for stormwater management. The plan was altered and refined in several areas. Approvals were received starting in November 1989 with the final approval given on January 23, 1990.

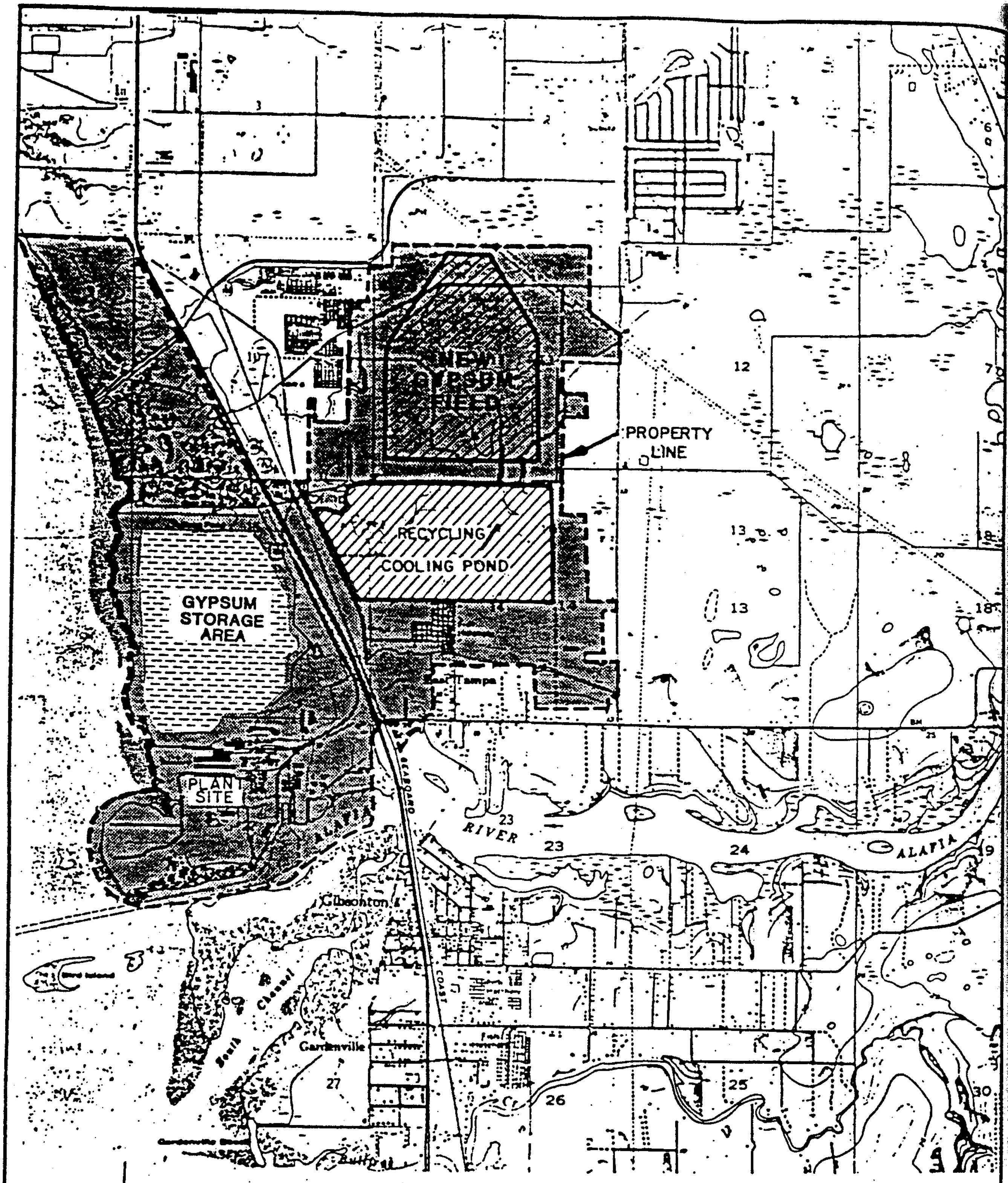
The following timetable was made a part of the permit:

OLD FIELD PREPARATION

EVENT	TIME OF COMPLETION
Plant approved to close old phosphogypsum disposal field	Closure Approval*
Drain water off old field and start to charge new field	Approval + 2 months
Complete charge new field	Approval + 6 months
Start to fill depression - old field	Approval + 3 months
Construct stormwater retention ponds	Approval + 5 months
Complete fill depression - old field	Approval + 6 months
Full use of new field	Approval + 6 months
Grade top of old field	Approval + 8 months
Let top settle and regrade as necessary	Approval + 8 months
Install outfall spillways	Approval + 10 months
Install membrane on old field	Approval + 11 months
Complete membrane installation	Approval + 12 months
Spread cover fill and topsoil	Approval + 13 months
Seed and mulch old field	Approval + 14 months

* Closure approval is the effective date of permit issuance or the date of receipt by the permittee of closure plan approval from the Hillsborough County Board of County Commissioners. (January 23, 1990)

LIST OF ILLUSTRATIONS



SITE LOCATION MAP

TOWNSHIP 30S, RANGE 19E

Ardaman & Associates, Inc.
Consulting Engineers in Soil Mechanics, Foundations, and Material Testing

CLOSURE PLAN
EXISTING GYPSUM STACK
GARDINIER, INC.-EAST TAMPA
HILLSBOROUGH COUNTY, FLORIDA

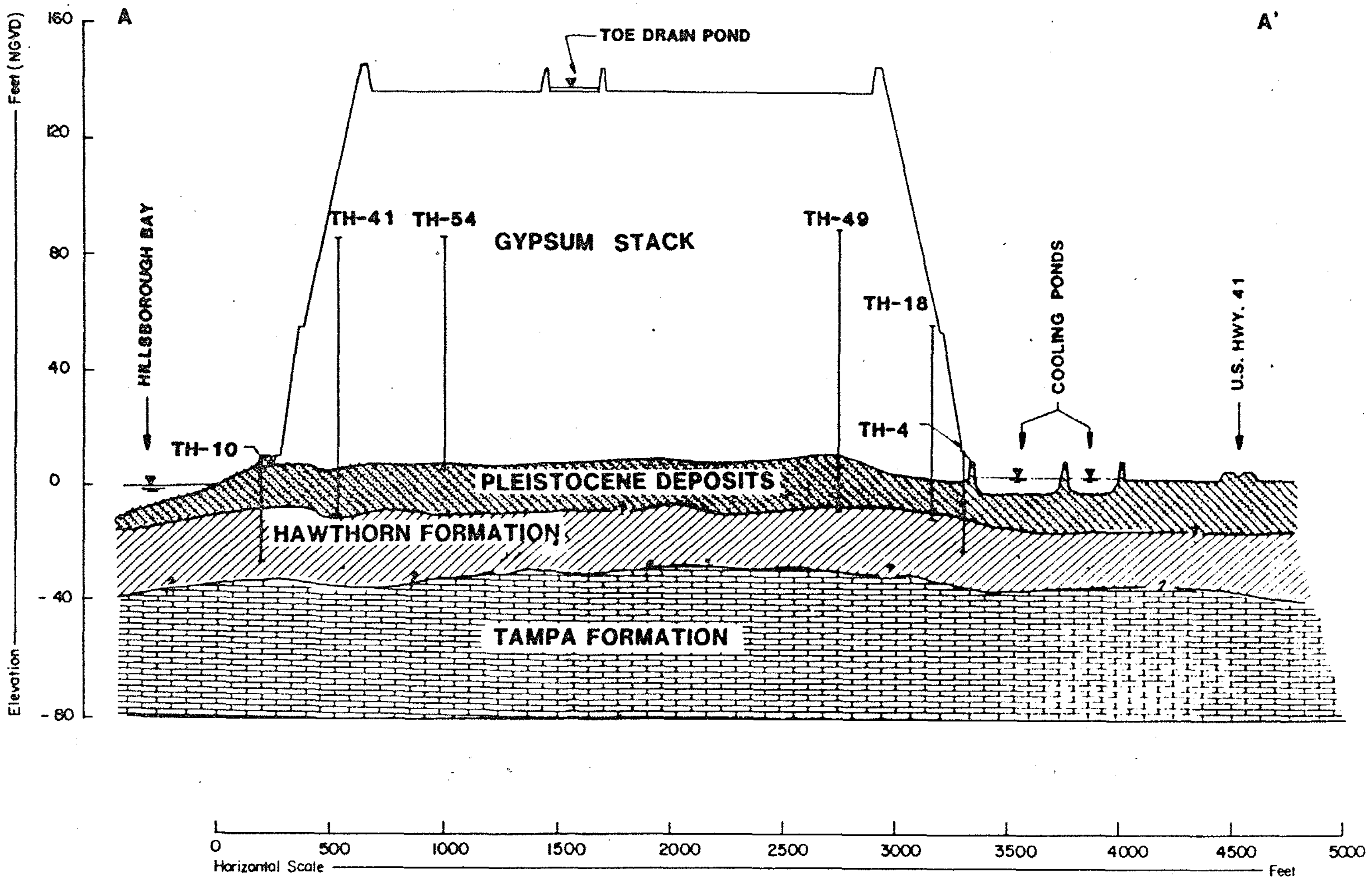
DRAWN BY: D.G.O.	CHECKED BY:	DATE: 12/7/88
FILE NO. 87-088	APPROVED BY: H.G. Stangland	

35304

SOURCE: USGS QUAD MAPS: BRANDON, FLA. (1969), GIBSONTON, FLA. (1969), RIVERVIEW, FLA. (1956), TAMPA, FLA. (1969).

FIGURE 1.1

WEST-EAST GEOLOGIC SECTION A-A'



TEST BORINGS PERFORMED BY WOODWARD-THORFINNSON & ASSOC. (REPORT DATED: OCT. 9, 1974).

OTHER SOURCE OF INFORMATION WAS TOPOGRAPHIC MAP OF GYPSUM STACK PROVIDED BY
GARDINIER, INC.

SOURCE: ARDAMAN, 1983

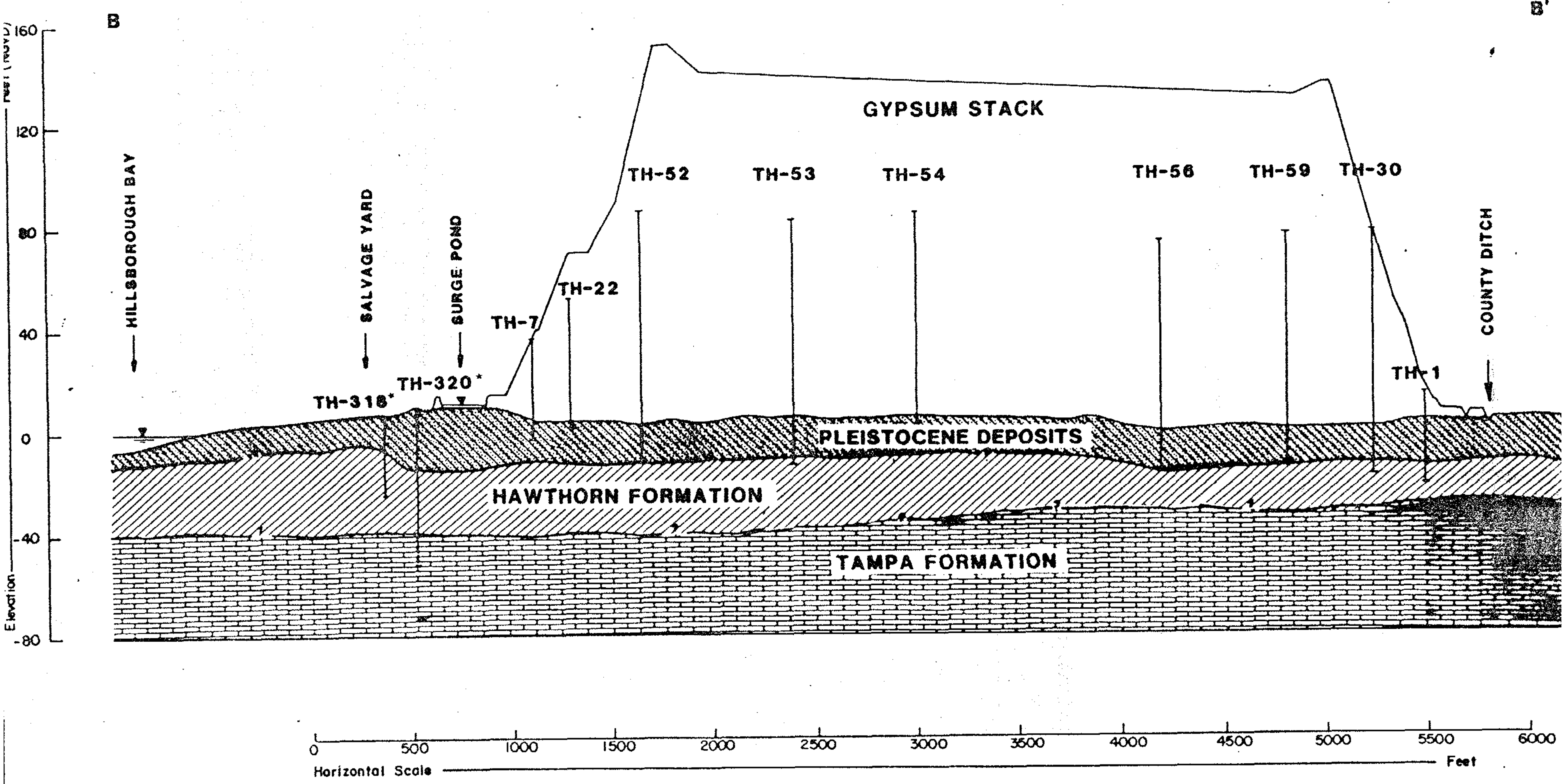
Ardaman & Associates, Inc
Consulting Engineers in Soil Mechanic
Foundations and Material Testing

CLOSURE PLAN
EXISTING GYPSUM STACK
GARDINIER, INC.-EAST TAMPA
HILLSBOROUGH COUNTY, FLORIDA

DRAWN BY N.A.G. CHECKED BY [illegible] DATE 12/7
FILE NO 87-088 APPROVED BY

FIGURE 1.2

SOUTH-NORTH GEOLOGIC SECTION B-B'



TH-10 : TEST BORINGS PERFORMED BY WOODWARD-THORFINNSON & ASSOC. (REPORT DATED: OCT. 9, 1974)

TH-320*: TEST BORINGS PERFORMED BY WOODWARD-CLYDE CONSULTANTS (REPORT DATED: SEPT. 23, 1976)

OTHER SOURCE OF INFORMATION WAS TOPOGRAPHIC MAP OF GYPSUM STACK PROVIDED BY GARDINIER, INC.

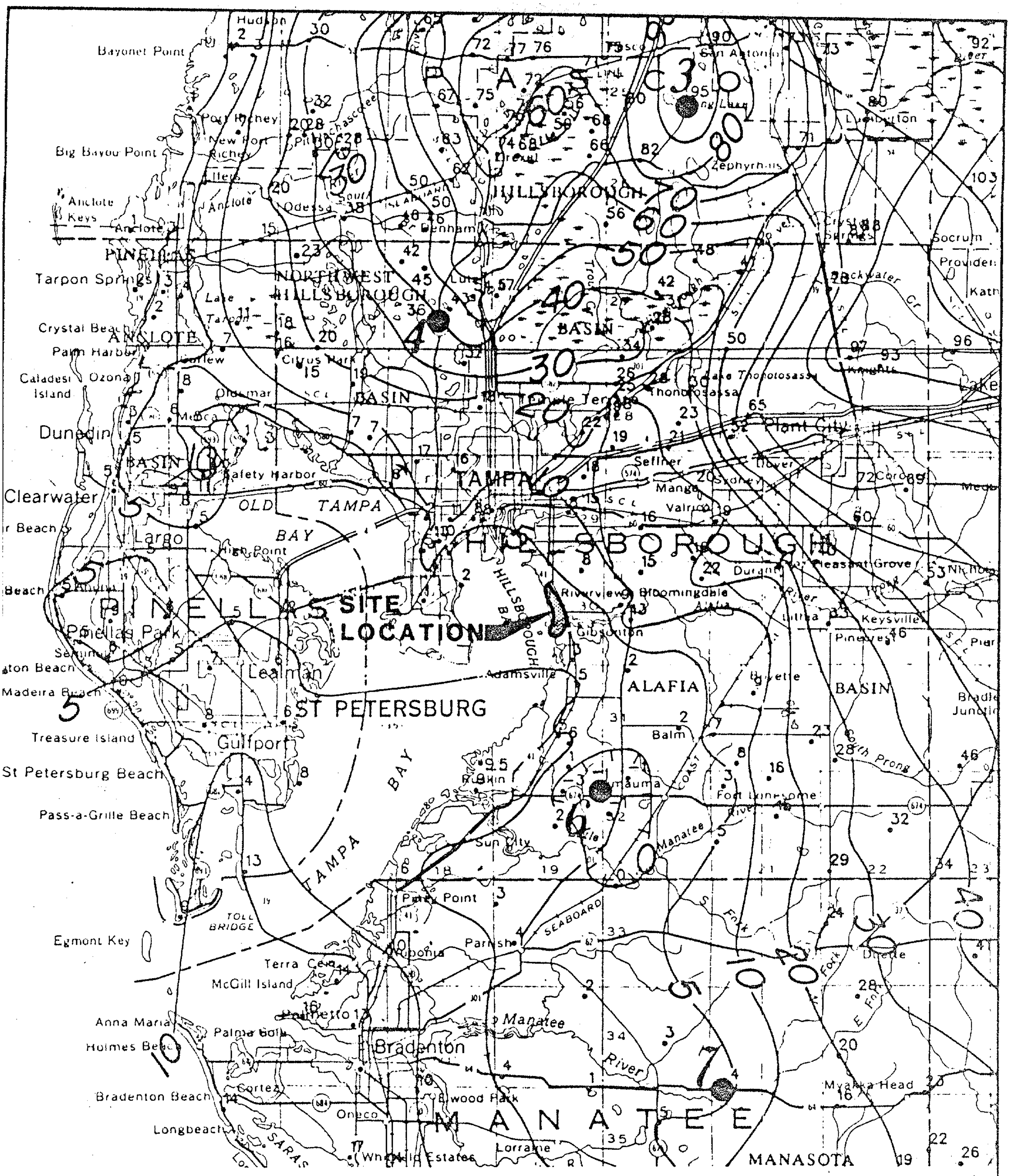
SOURCE: ARDAMAN, 1983

Ardaman & Associates, Inc
Consulting Engineers in Soil Mechanics
Foundations, and Material Testing

CLOSURE PLAN
EXISTING GYPSUM STACK
GARDINIER, INC.-EAST TAMPA
HILLSBOROUGH COUNTY, FLORIDA

DRAWN BY N.A.G.	CHECKED BY KSK	DATE 12/7/
FILE NO 87-088	APPROVED BY Rangland	

FIGURE 1.3



POTENTIOMETRIC SURFACE OF THE FLORIDAN AQUIFER
MAY 1987

N

0 5 10

SCALE——FEET

SOURCE: SOUTHWEST FLORIDA WATER MANAGEMENT DISTRICT

Ardaman & Associates, Inc.
Consulting Engineers in Soil Mechanics, Foundations, and Materials Testing

CLOSURE PLAN
EXISTING GYPSUM STACK
GARDINIER, INC.-EAST TAMPA
HILLSBOROUGH COUNTY, FLORIDA

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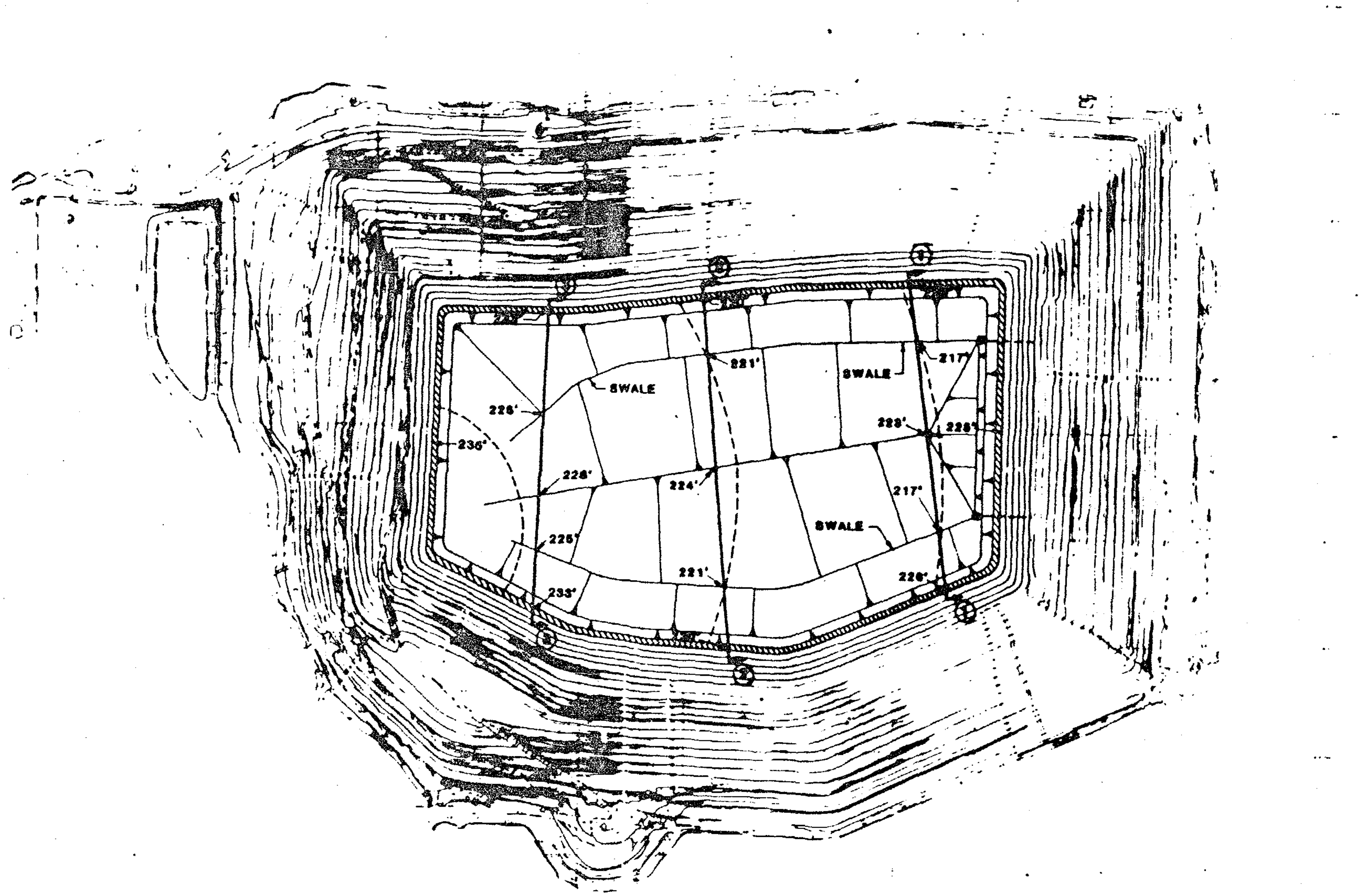
FIGURE 1.4



GRADING PLAN FOR GYPSUM SURFACE PRIOR TO PLACING TOP LINER

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CLOSURE PLAN
EXISTING GYPSUM STACK
GARDINIER, INC.-EAST TAMPA
HILLSBOROUGH COUNTY, FLORIDA

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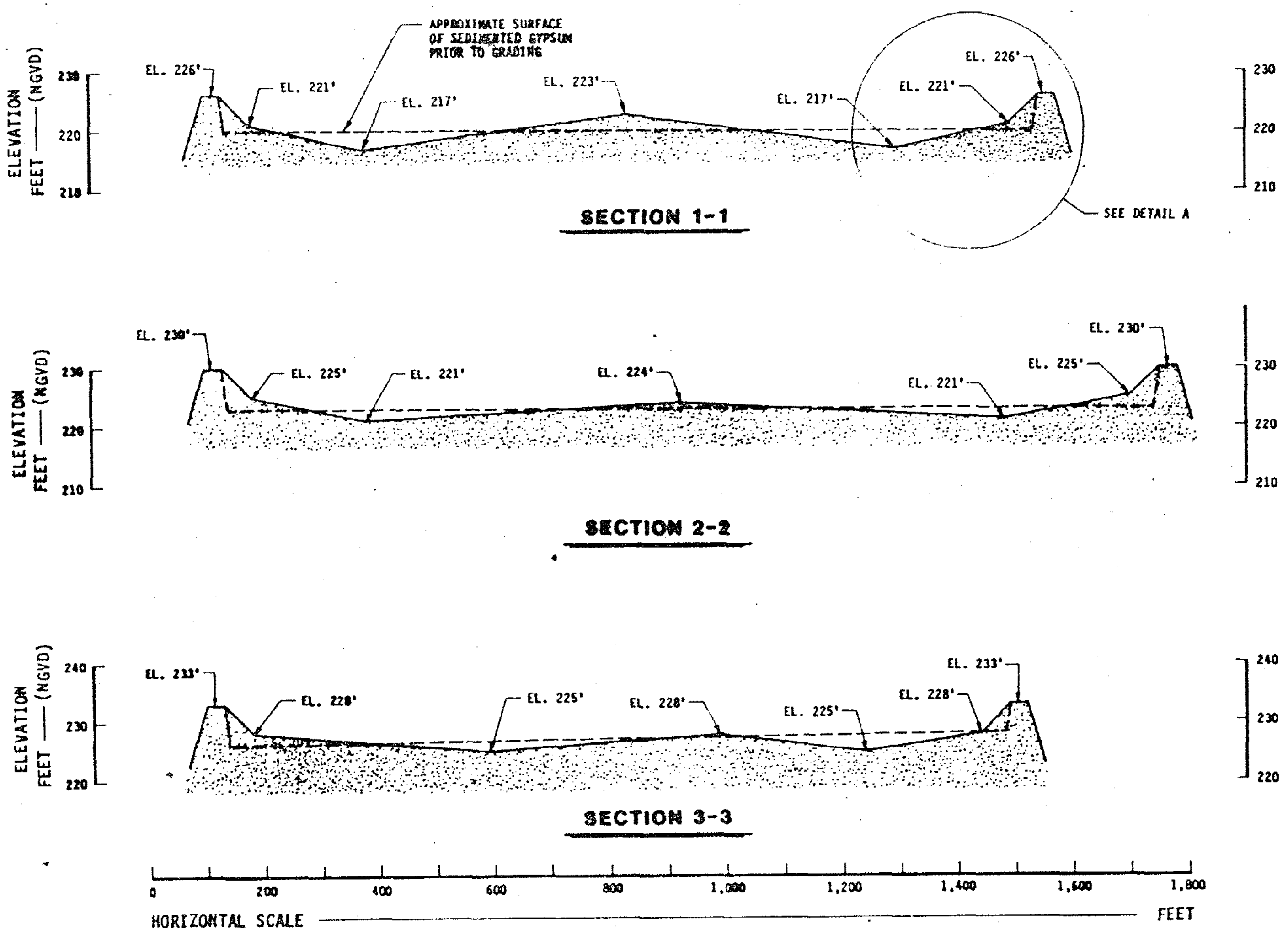
FIGURE 1.5



CROSS SECTIONS FROM GRADING PLAN FOR GYPSUM SURFACE PRIOR TO PLACING LINER

Ardaman & Associates, Inc.
Consulting Engineers in Soils, Hydrogeology, Foundations, and Materials Testing

CLOSURE PLAN
EXISTING GYPSUM STACK
GARDINIER, INC.-EAST TAMPA
HILLSBOROUGH COUNTY, FLORIDA

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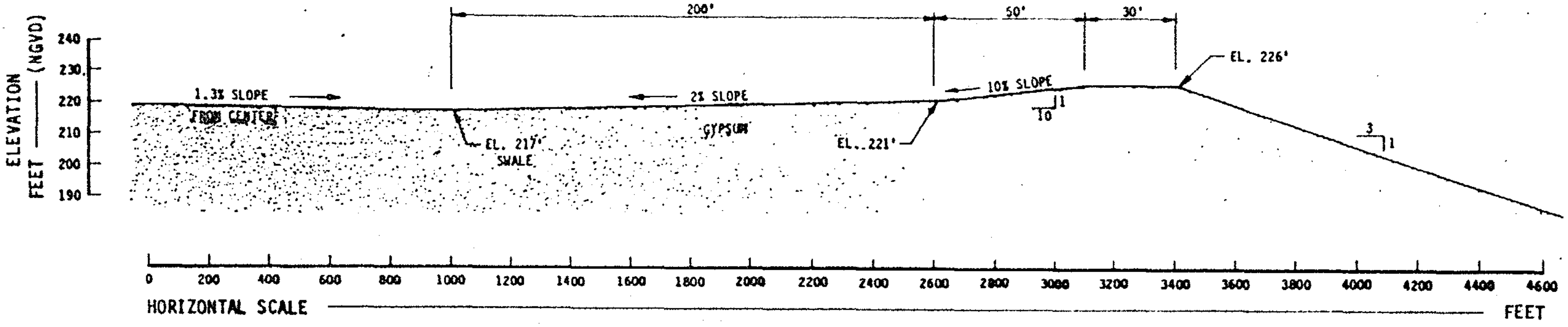
FIGURE 1.6



DETAIL A

TYPICAL GRADED SLOPES ON TOP OF GYPSUM
STACK PRIOR TO PLACEMENT OF TOP LINER

DETAIL A FROM GRADING PLAN CROSS SECTIONS

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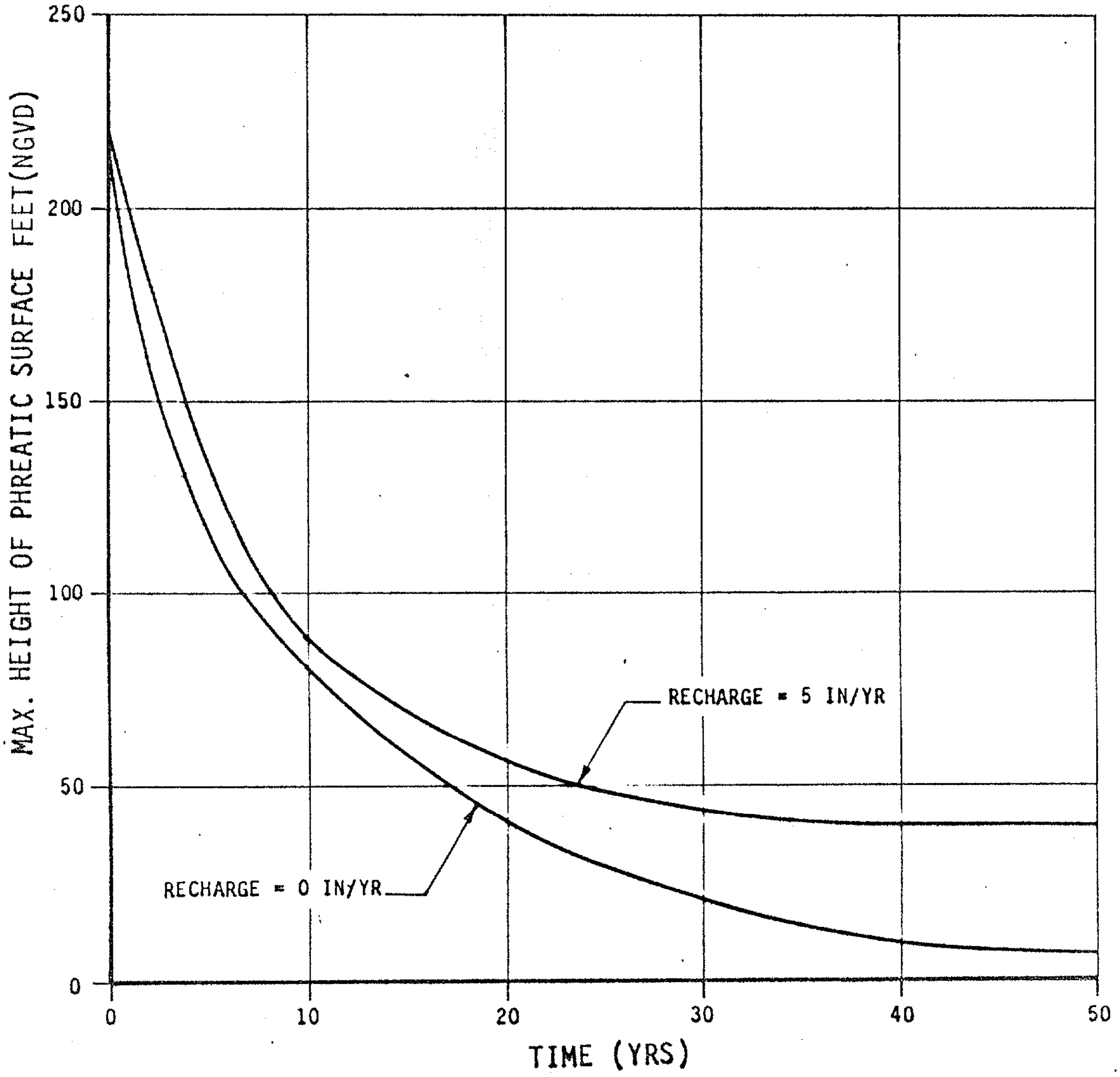
Foundations, and Materials Testing

CLOSURE PLAN
EXISTING GYPSUM STACK
GARDINIER, INC.-EAST TAMPA
HILLSBOROUGH COUNTY, FLORIDA

DRAWN BY | CHECKED BY | DATE
FILE NO 87-028 | APPROVED BY

FIGURE 1.7



HEIGHT OF GYPSUM STACK PHREATIC SURFACE VERSUS TIME

Ardaman & Associates, Inc.
Consulting Engineers in Soil Mechanics, Foundations, and Materials Testing

CLOSURE PLAN
EXISTING GYPSUM STACK
GARDINIER, INC.-EAST TAMPA
HILLSBOROUGH COUNTY, FLORIDA

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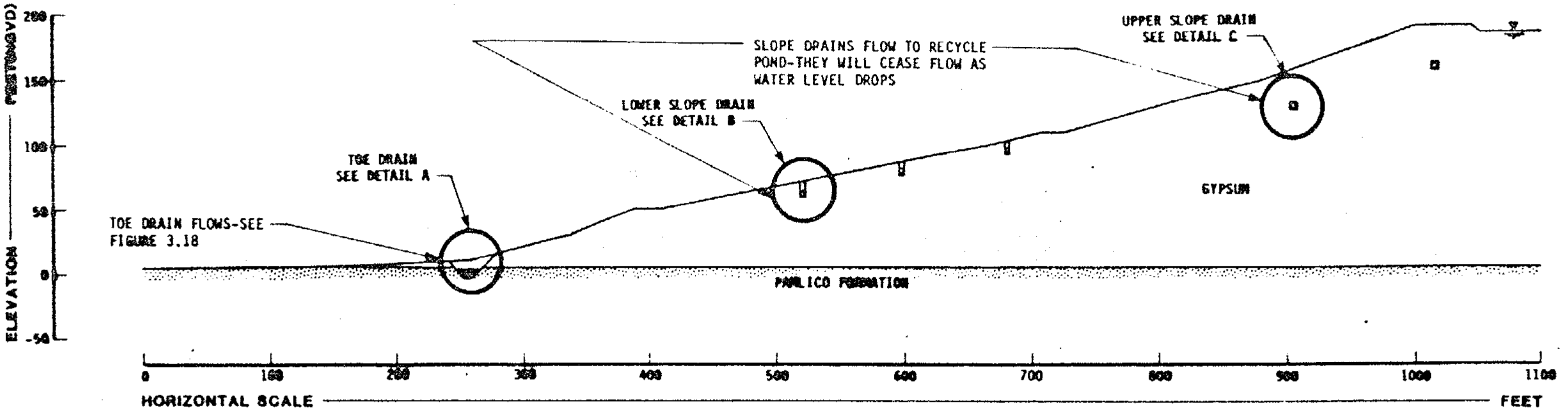
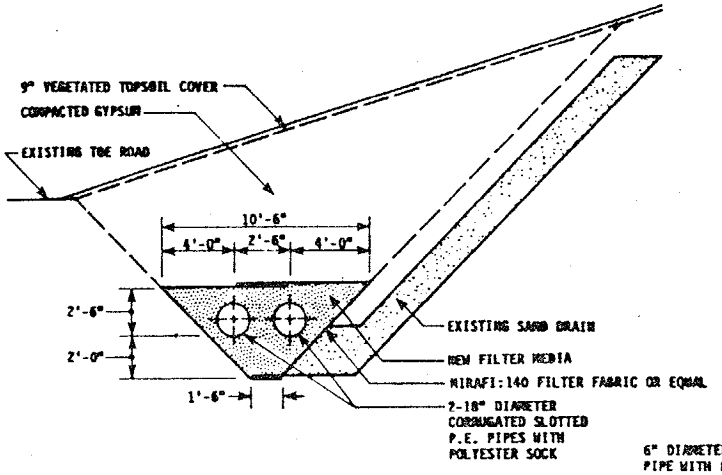
N82070

FIGURE 1.8

CROSS SECTION ④ - ④

WEST WALL OF GYPSUM STACK
SHOWING SLOPE AND TOE DRAIN GEOMETRY





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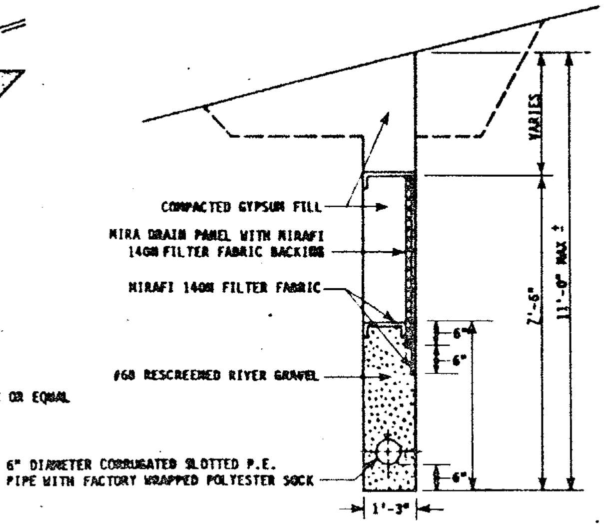

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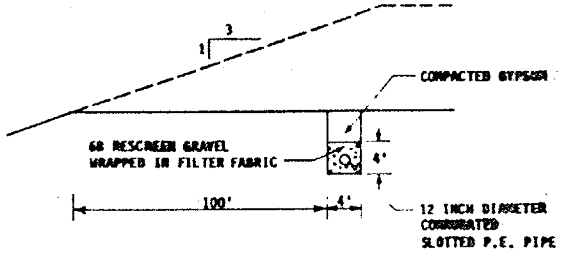

DETAIL C
(NOT TO SCALE)

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Consulting Engineers in Soil Mechanics,
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CLOSURE PLAN
EXISTING GYPSUM STACK
GARDINIER, INC.-EAST TAMPA
HILLSBOROUGH COUNTY, FLORIDA

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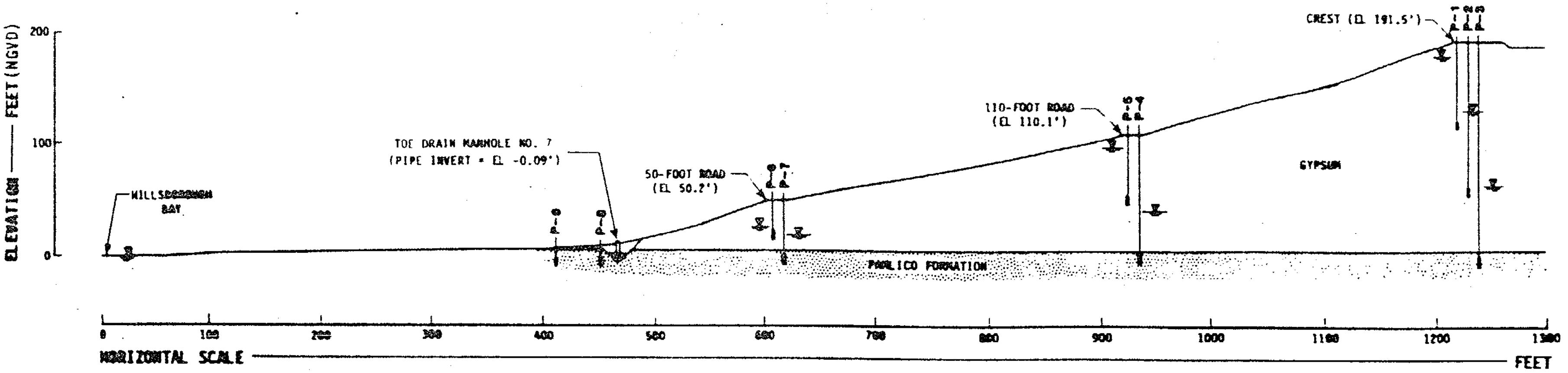
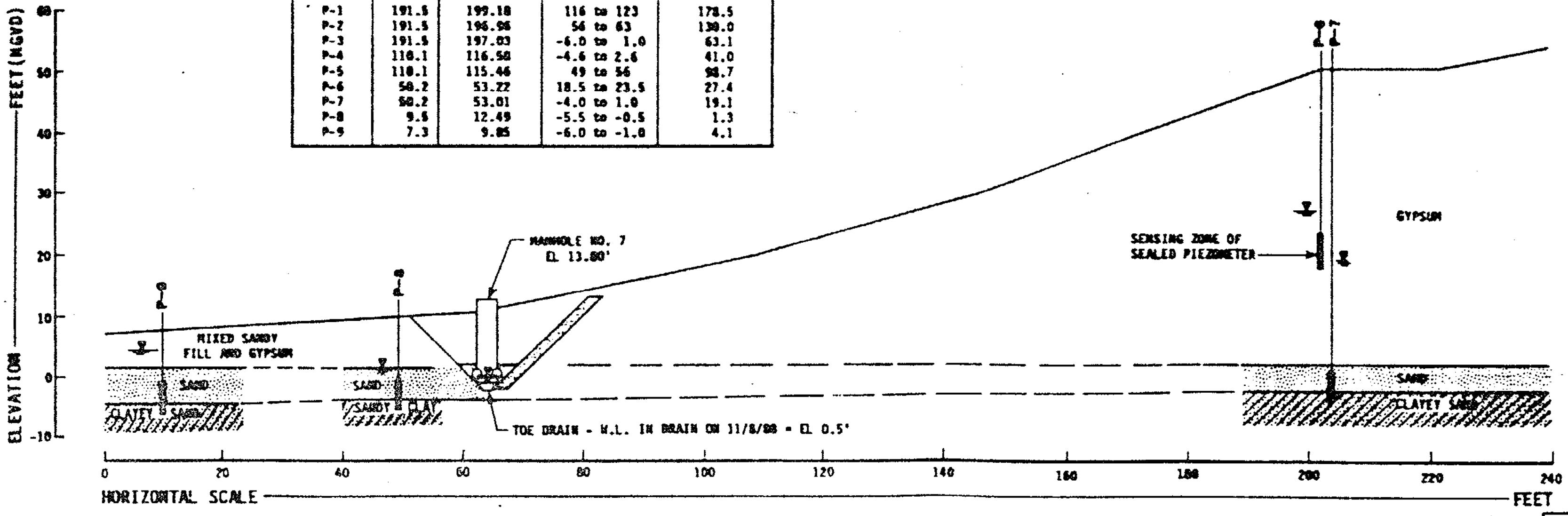
REVISED

FIGURE 1.9

CROSS SECTION ① - ①



PIEZ. NO.	ELEVATIONS - FEET (NGVD)			
	GROUND	TOP OF PIPE	SENSING ZONE	WATER 11/8/88
P-1	191.5	199.18	116 to 123	178.5
P-2	191.5	196.96	56 to 63	130.0
P-3	191.5	197.03	-6.0 to 1.0	63.1
P-4	110.1	116.58	-4.6 to 2.6	41.0
P-5	110.1	115.46	49 to 56	98.7
P-6	50.2	53.22	18.5 to 23.5	27.4
P-7	50.2	53.01	-4.0 to 1.0	19.1
P-8	9.5	12.49	-5.5 to -0.5	1.3
P-9	7.3	9.85	-6.0 to -1.0	4.1



CROSS SECTION (1A) - (1A)

PIEZOMETER INSTALLATION DETAILS

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CLOSURE PLAN
EXISTING GYPSUM STACK
GARDINIER, INC.-EAST TAMPA
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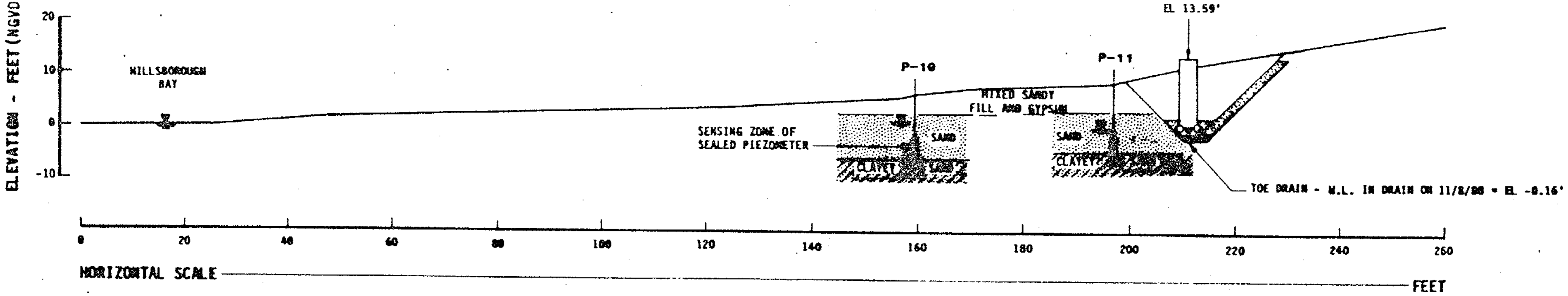
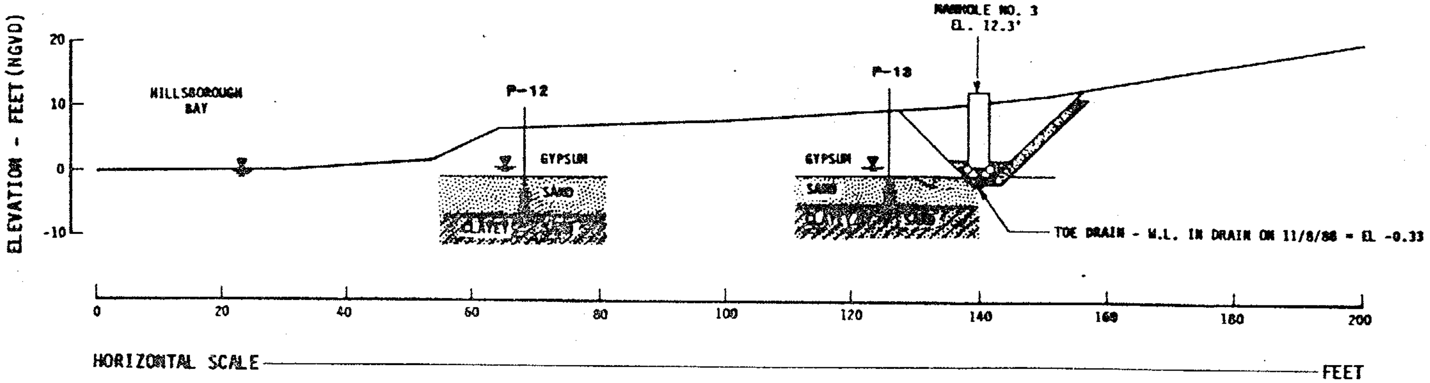
FIGURE 1.10

CROSS SECTION ② - ②



PIEZ. NO.	ELEVATIONS - FEET (NGVD)			
	GROUND	TOP OF PIPE	SENSING ZONE	WATER 11/8/88
P-10	7.0	9.60	-6.5 to -1.5	1.35
P-11	8.6	11.93	-6.0 to -1.0	0.35
P-12	7.0	9.86	-8.0 to -3.0	0.06
P-13	9.1	11.85	-7.0 to -2.0	0.75

CROSS SECTION ③ - ③



PIEZOMETER INSTALLATION DETAILS

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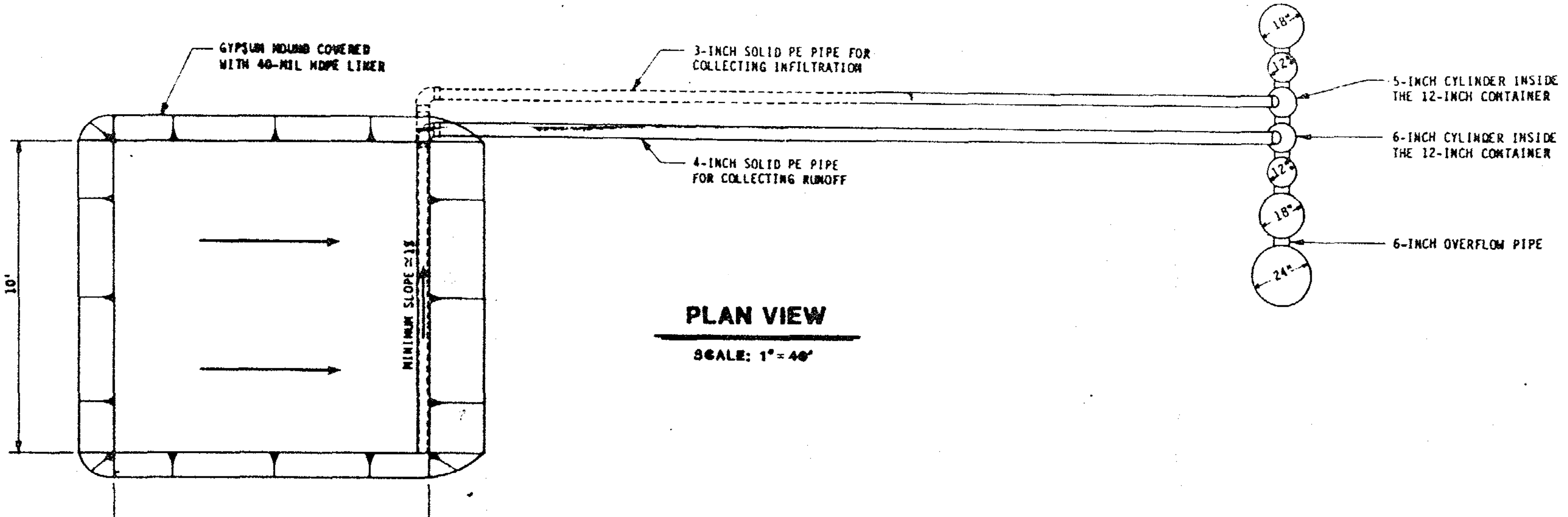
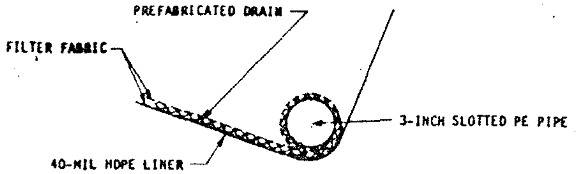
FIGURE 1.11



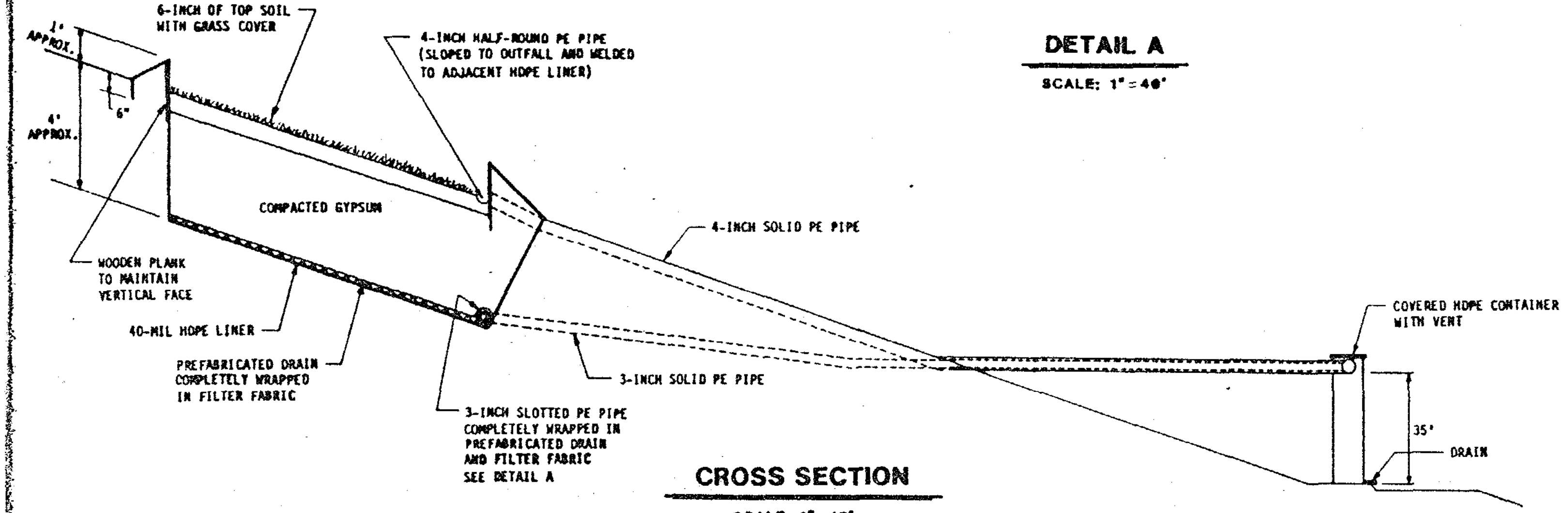
PLAN VIEW

SCALE: 1" = 40'



DETAIL A

SCALE: 1" = 40'



CROSS SECTION

SCALE: 1" = 40'

SLOPE INFILTRATION TEST APPARATUS

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GARDINIER, INC.-EAST TAMPA
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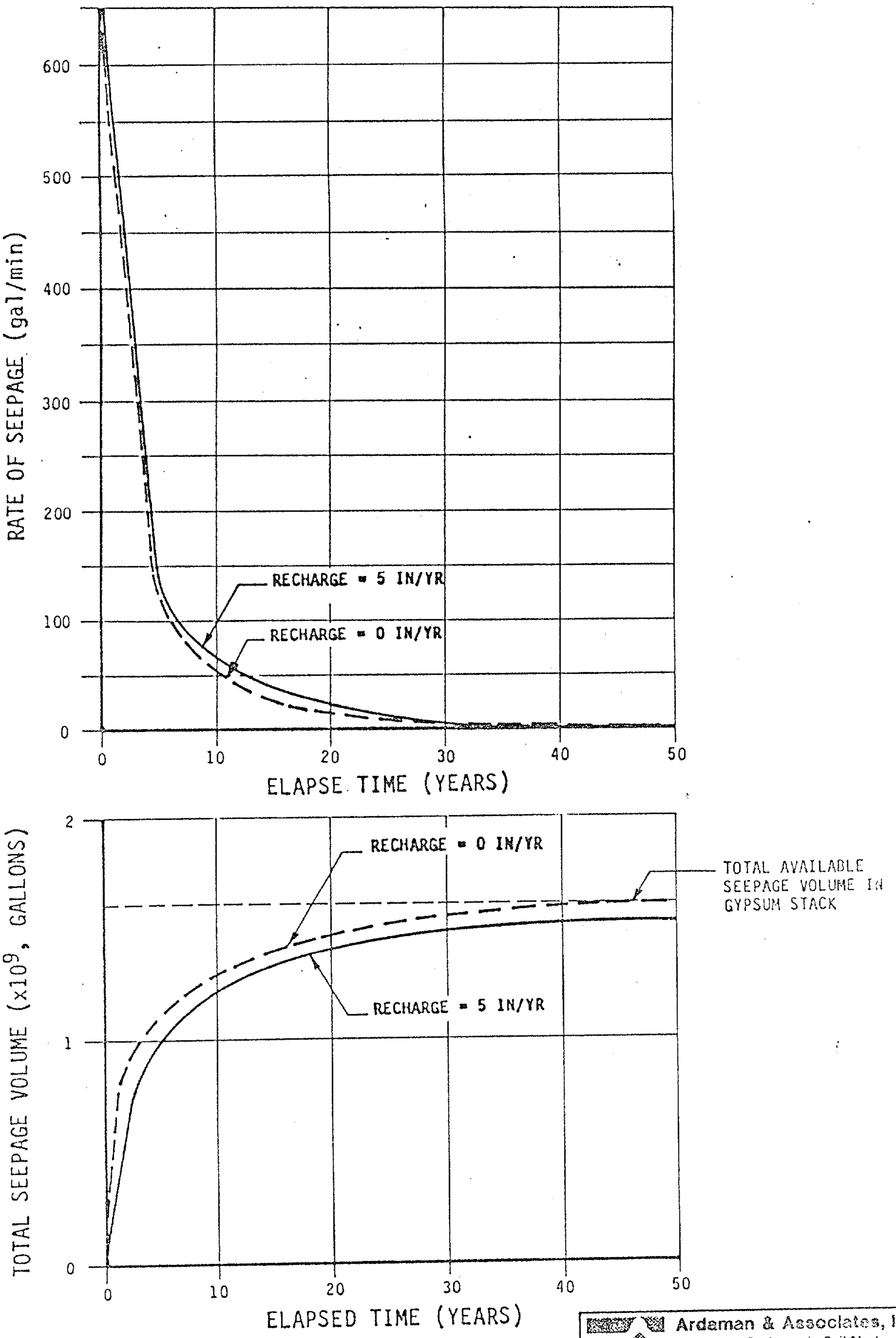
FIGURE 1.12



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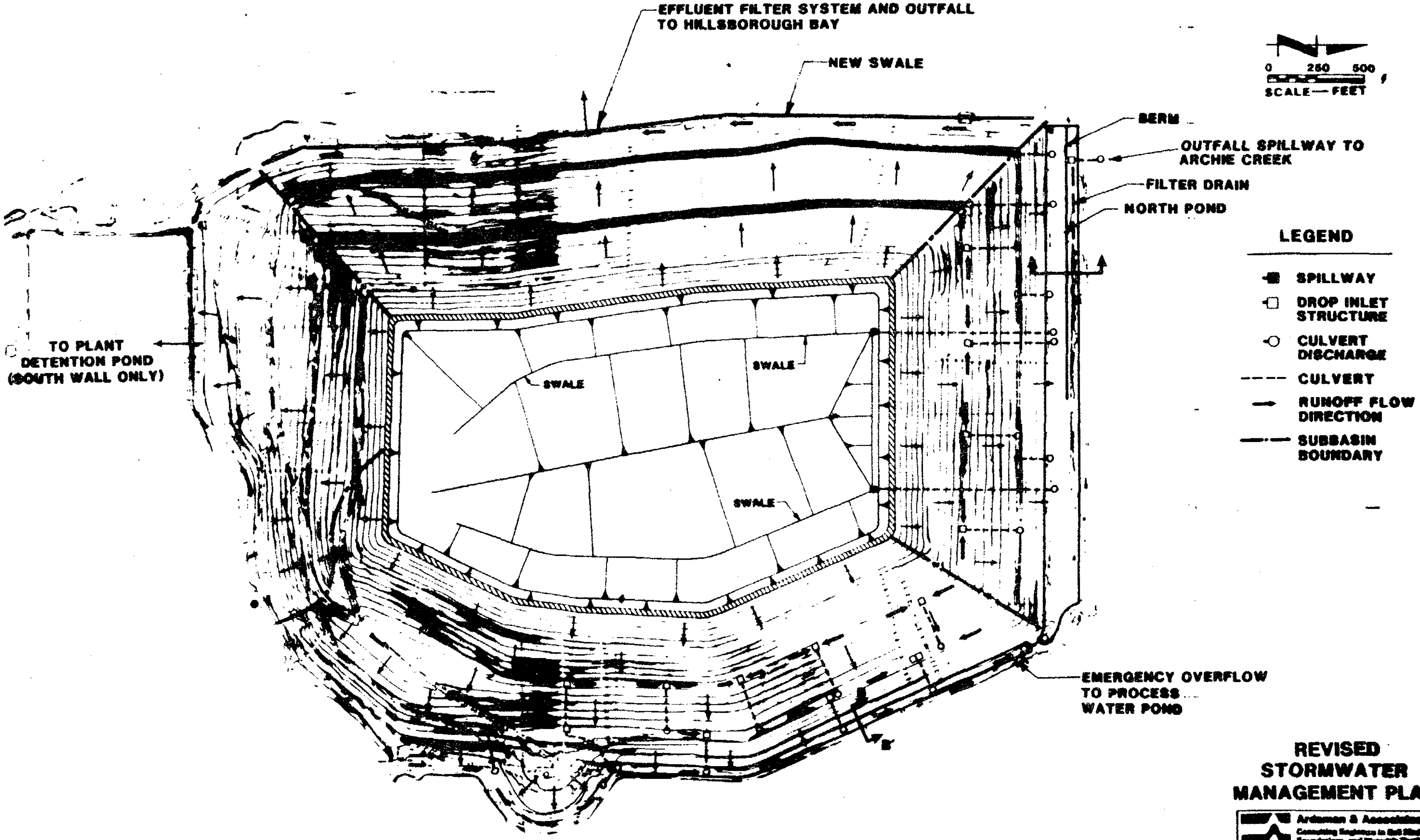
DRAINAGE OF GYPSUM STACK

FIGURE 1.13



REVISED STORMWATER MANAGEMENT PLAN

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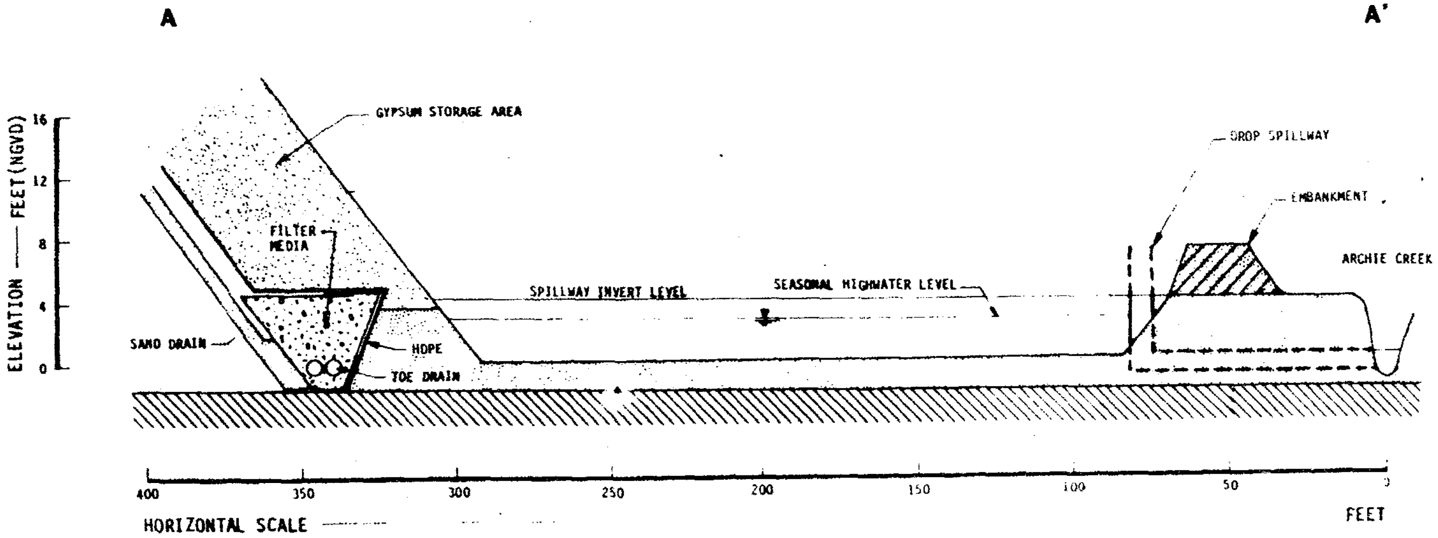
EXISTING GYPSUM STACK
GARDINIER, INC.-EAST TAMPA
HILLSBOROUGH COUNTY, FLORIDA

87-086

FIGURE 1.14



NORTH POND A-A'

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EXISTING GYPSUM STACK
GARDINIER, INC.-EAST TAMPA
HILLSBOROUGH COUNTY, FLORIDA

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FIGURE 1.15

TABLE A

SUBBASIN AREAS

Location	Area (acres)
North Slope	37
East Slope	76
Upper West Slope	55
Lower West Slope	22
South Slope	39
Top Area	99
Total	328

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PILOT-SCALE DEVELOPMENTS IN PRODUCTION OF SOIL CHALK FROM PHOSPHOGYPSUM

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ABSTRACT

The technological idea of the waste-free method production of the NPK fertilizer and soil-chalk with complete phosphogypsum utilization on the 1th International Symposium on Phosphogypsum (Buena Vista - 1980) was presented. This process depends on technological connection of the wet-process phosphoric acid, fertilizer, ammonia and conversion phosphogypsum by CO_2 and NH_3processes.The results of the pilot plant production of the soil chalk from phosphogypsum are presented. This process was realized in the semi-technical plant located in Chemical Works “Police” of 1 t soil-chalk per hour capacity. The semi-technical plant was connected with phosphoric acid plant. The phosphogypsum was converted to calcium carbonate and solution of ammonium sulfate by acting gaseous CO_2 and NH_3 in single - stage process. Pilot scale investigation have shown that the process occurs with 92-94 efficiency and the chalk produced contains more than 70% $CaCO_3$ (counting the dry mass> and may be successfully used as a soil chalk. The precipitated calcium carbonate was filtered off using automatic filter press and obtained filter cake contained below 20% of the moisture and was suitable for direct spreading into soil with fertilizer digging reels. In the process a part of the P_2O_5 forms contained in phosphogypsum is recovered, because the part passes to the ammonium sulfate solution during conversion process but a main part in the form of dicalcium phosphate, assimilable by plants. In fertilization of chalk/hec, (acidic soils), can additionally be introduced to the soil. Finally, the total amount

P_2O_5 contained in the phosphate raw materials is delivered to the soil for fertilzation. The greenhouse and field studies have been completed in which soil-chalk from phosphogypsum have been evaluated agronomically. Several prediction of this product agronomic effectiveness can be made with a fairly high degree of confidence.

The pilot-plant test production have shown that in the single-stage conversion process phosphogypsum may be utilized in the fertilizer works where ammonia plant is located. This process is economically attractive because 20% H_2SO_4 comsumption is decreased, all forms of P_2O_5 are agronomically available and deacidifying fertilizer (chalk) is produced instead of phosphogypsum.

INTRODUCTION

The total phosphogypsum utilization in the economic processes is technically impossible and utilization the waste phosphogypsum produced in the wet-phosphoric acid process in the additional process it is not the only way to cancel this problem. The other way depends on technological modification of the phosphate raw material processing. Institute of Inorganic Technology and Mineral Fertilizer Technical University of Wroclaw and Chemical Works “Police” (Poland) have developed a process for production of compoud fertilizer NPK simultaneously with soil-chalk instead of phosphogypsum. The technological idea of this waste-free method on the first International Symposium on Phosphogypsum (Buena Vista 198O) was presented. This process (Schroeder J.,Gorecki H.,1980) depends on the coupling the wet-process phosphoric acid plant, ammonia plant and conversion phosphogypsum process by acting ammonia and carbon dioxide. The idea of this process is illustrated in Figure 1. The technological system consists of combining the phosphate raw material acidulation process (A) (Schroeder, Gorecki and Szczygiel, l977; Schroeder et al., l977; Gorecki, l98O; Hoffmann, l989) conversion of the phosphogypsum (B) (Schroeder, Synowiec and Gorecki, l978; Gorecki, Patrzek, l986; Gorecki et al., 1989) production of fertilizer (C) (Gorecki, 1980;Schroeder et al., 1974) and ammonia process in the circulation system.

The phosphate raw material is decomposed in a typical dihydrate plant in the presence of ammonium ion according to the reaction:

$$Ca_5F(PO_4)_3 + n(NH_4)_2SO_4 + 4H_2SO_4 + 10H_2O \xrightarrow{70-80°C} 2NH_4H_2PO_4 + H_3PO_4 + (n-1)(NH_4)_2SO_4 + 5CaSO_4 \cdot 2H_2O + HF$$

eq.(1)

at $1 \leqslant n \leqslant 4,5$

Ammonium sulfate solution is produced in the process of converting phosphogypsum into chalk using ammonia and carbon dioxide according to the reaction:

$$CaSO_4 \cdot 2H_2O + 2\ NH_3 + CO_2 \longrightarrow CaCO_3 + (NH_4)_2SO_4 + H_2O$$

eq.(2)

The filtrate obtained in this concentration process, 35-42% of $(NH_4)_2SO_4$ mass, is used for washing the filter cloth and the phosphogypsum filter cake,whereas a part of the filtrate is introduced directly into the NPK fertilizer production.

The phosphogypsum produced in the decomposition process is washed counter-currently on the filter Sulfuric acid is introduced to the washing liquid (Schroeder et al.,1982) in the next to last washing area. The amount of its constitutes is 10-20% of the sulfuric acid cosumed in acidulation process. The presence of ammonium ion in the liquid during acidulation has number of advantages. One of them is the increase of calcium sulfate dihydrate crystalization field which is caused by a shift of the phase transition line of $CaS0_4 \cdot 2H_20$ and $CaS0_4 \cdot 1/2H_2O$* by about 10-30 deg and also due to more favourable conditions for an increase in phosphogypsum crystals.

Acidulation process using the mixture of sulfu ric acid and ammonium sulfate was successfully tested in the plant of 110 th t P_20_5/year (Gorecki, 1980, Hoffmann 1989) and NPK fertilizer 14:14:14 grade in industrial scale (Schroeder et a1. 1988).

On the basis of the bench scale investigation (Gorecki H.,Patrzek F.,1986) the pilot plant production of the soil-chalk from phosphogypsum was tested.

EXPERIMENTAL SECTION

The two-stage methods of converting sulfate mineral raw materials (e.g. anhydrite) into chalk and ammonium sulfate used in industry up to this date are inconvenient, particulary when phosphogypsum is used as a raw material.

This, in particular, concerns the problem of receiving NH_3 and CO_2 absorption heat in the stage of making $(NH_4)_2CO_3$ solution, the difficulty with water balance in the second-stage, the concentration and crystallization of $(NH_4)_2SO_4$, as well as problems connected with $CaCO_3$ crysallization.

Despite of the fact that the conversion methods are divided into so-called liquid and gaseous methods (Slack,1968), there is a lack of concrete technological solution in the gaseous process (single-stage). It was only the Dutch firm, Continental Engineering Co (1970), that presented a conception of solving this problem though without any technological details. There have been no reports yet concerning the implementation of this process in industrial production. The solution consists of rector application in the form of tower while phosphogypsum pulp is fed into the reactor from the preliminary mixer-reactor and series-connected reactors into which gaseous NH_3 and CO_2 are introduced.

The absorption and reaction heat is collected by means of series-located mambrane coolers (behind the absorption reactor).

In order to avoid the inconvenient of the liquid method and the application of phosphogypsum as raw material, a new conception was developed and a device designed, the technological workability of which was tested in pilot plant.

SEMI-TECHNICAL PLANT

The pilot tests of phosphogypsum conversion process were carried out in pilot-plant located in the wet phosphoric acid plant in Police Works (Northern Poland).Its schematic diagram is presented on Fig.2. The basic apparature of this installation is a conversion reactor (1).The reactor volume is 16 m^3,and its working volume is about 10 m^3. The mixing and suspension circulation is performed by a circulation pump AMRM 60 Ensival type. The reactor and circulation pipes are made of acid resistant steel, Uranos. Gaseous ammonia and carbon dioxide were added into the circulation pipe of the reactor under 0,2MPa pressure. The plant was consisted of a tank (4) for phosphogypsum repulping with ammonium sulfate solution (washings), the FPAKM 25 filter press (2)(made in USSR), filtrate tank (3),water scrubber (5) and water condenser (6). During these pilot tests CO_2 liquid was added from a railway tank (8) through the vaporizer (7) as a gas under 0,2 MPa, and gaseous NH_3 was added from an NPK fertilizer plant combined with wet phosphoric acid plant.

The conversion reaction and gas absorption heat was received adiabatically. The suspension containing 18-25% of calcium carbonate in ammonium sulfate solution was passed into the filterpress. After being washed with water, the filter cake of the chalk contains about 20% water.. Ammonium sulfate solution of concentration of 35-42% $(NH_4)_2S0_4$ was added to the next to last phosphogypsum washing area in the wet phosphoric acid plant and was used for acidulation.

The vapours formed in the conversion reactor were absorbed in a water scrubber and a barometric condenser connected with the adiabatic evapourizer used for cooling the phosphogypsum pulp in the industrial wet phosphoric acid plant.

The intensity of CO_2 and NH_3 flow was measured by means of measurement reducers. Signals from APQ converters proportional to the pressure difference on the reducer were sent to NSK recorder and ELP-11 electronic flow counter. Pneumatic pressure senders enabled remote control of the valves equipped with pneumatic membrane servo-motors with positional controllers.

The signalization of transgressing three filling levels of the reactor was recorded by radioisotopic transmitters, UPR-11 type 2-4 (made in Poland), receiving signals from the heads which have isotopic radiation sources. Pulp temperature in the reactor was measures by means of resistance thermometer which signal was sent to NSK recorder. The pressure in the reactor was measured with manometer having pneumatic pressure converter of range of 100 to kPa. Chalk suspension pH was measures by means of pH-meter with flow heads.

Sensorrs' indications were recorded in the steering station of the installation and in the steering station of the filtration press. The activity of FPMAK-25 filter press was estimated in a programmed manner, designating the filtration, washing and drying time in cyclical repeated operations.

ANALYTICAL CONTROL

The composition of the suspension collected from the reactor in one hour time was under analytical control, investigating independently liquid and solid phase composition. The composition of the filtrates and samples of the chalk was determined, as well as codensates composition from barometric closures of the scruber and barometric vapourizer.

Following contents were determined in the analysed liquids:

- -of sulfate ion (the titration method applying $BaC1_2$ in the presence of nitrochromazo),
- -of dissolved ammonia (with the ion-selective electrode Orion 95100 - direct measurement),
- -of ammonium ion (electrode Orion 95100 after adding NaOH),
- -of carbonate compounds (the electrode for measuring CO_2 concentration - Orion 950200),
- -of phosphate ions (the vanadium-molybdenum colorimetric method),

The composition of the precipitates was determined as follows:

- -of sulfates (by the weight method after $BaSO_4$ precypitation, and by the enthalpymetric method applying automatic microcalorimeter Dithermanal with microprocessor Thermorobot - made in Hungary),
- -of phosphates (P_20_5 dissolved in water and independently in citric acid was determined by the vanadium-molybdenum method),
- -of calcium (on the atomic spctrophotometer AAS1-made in DDR),
- -of iron (by the calorimetric method applying colour reaction with sulfosalicylic acid and the atomic spectrometry method).

Chalk moisture and $CaCO_3$ (or CO_2) content were determined by the thermogravimetric analysis method carried out on derivatograph MOM Budapest (Hungarian production).
Filtration properties of fertilizer chalk were appraised in a comparative way with the immersed filtration probe, measuring filtration time of a constant filtrate's volume. The crystal sizes distribution curves where determined using Sartorius sedimentation device.

PILOT-PLANT SOIL CHALK FROM PHOSPHOGYPSUM PRODUCTION

The pilot-plant process (Table 1) consisted of the periodic initiated process which was conducted in a batch way (a),the process realization phase at an increase of ammonium sulfate concentration in the liquid phase (b),and the production phase realized in the stable process parameters(c).

In the period (a),phosphogypsum suspension was formed to reach the constant level of the liquid (L) to solid (S) phase ratio-Reactor (1) was filled with a part of the suspension to 3L height, and decrease of suspension in the tank (4) was completed by introducing phosphogypsum and water in the proper amount so as to secure constant value of the L/S ratio. Having filled the reactor, NH_3 was added to it in 300 s portions, and CO_2 was added while maintaining the mole ratio $NH_3/C0_2=2,05$. The process was carried out for 6 hour As a result, ammonium sulfate concentration in the aqueous phase increased to 12,6% $(NH_4)_2SO_4$, and the L/S ratio decreased to the value of 7,98. The periodic way of the process realization enabled convertion obtainment of 88,6% degree.

In the phase (b) the ammonium sulfate concentration increase occurred to 35-40% $(NH_4)_2SO_4$ and L/S ratio to the level of 3,2-3,8 with the assumption that the process is realized in a continuous manner and with the complete recycling of the filtrate to the process. This intention was realized by feeding the filtration press (2) from the reactor with chalk suspension of 2,4m^3 volume, which is the volume contained between 3L and 2L level. The filtrate from the filter press was sent to tank (4) to which 1000 kg of phosphogypsum were intoduced in each one-hour cycle. Rinsings from washing of the chalk were sent, in this period of the process, to the phosphoric acid plant.

In this period of the process, the pulp temperature was maintained at 55-55^{0}C and pressure at 0,05 MPa. Fig.3 presents concentration variability of ammonium sulfate and carbonates contained in the liquid phase as dependent on time; and in Tabl.1, basic process parameters are given.

After stabilization of the ammonium sulfate concentration at the level of 38-49% $(NH_4)_2SO_4$, process (c) was started, consisting of recycling the washings tsphoric acid installation.

The applied absorption system ensures total absorption of ammonia in the scrubber (2.,Fig.2), absorbing mainly acidic vapours from the wet phosphoric acid plant. Recorded at equal time intervals, the ammonia concentrations in the condensate from the absorption system permit a competent evaluation of the degree of ammonia desorption $\Delta NH_3(\%)$, determined as a ratio of the desorbed ammonia to the total ammonia introduced to the conversion process.

Tabl.2 presents the value of the regression coefficient of the equation, which determines the dependence of the NH desorption degree on the process, selected on the basis of the correlation analysis. The estimator ($\Delta \widehat{NH}_3$) was calculated by the least square method. On the basis of the equation, the dependence of the degree of ammonia desorption on temperature (Fig.4) and on the concentration of free ammonia contained in the liquid phase of the reaction pulp (Fig.5) under 0,5 MPa pressure was determined.

It has been found that it is possible to maintain desorption at the level of 1-2% with respect to the quantity of ammonia introduced into the reactor system using an adiabatic cooling system. The only requirement is to maintain the temperature in the range of $50-52^{0}$C.Desorption of ammonia in such an amount reveals no problem, since there is a possibility of using condensates to washing off chalk precipitates and phosphogypsum, and thus ammonium ion as a component of the rinsings is recycled to the technological process.

The realization of the pilot-plant process in such a way constitutes a reliable test for technological feasibility of the one-stage process.

Tab.3 presents average soil chalk composition after drying, at the ammonium sulfate concentration in the liquid phase of 40% $(NH_4)_2SO_4$.Fig.6 shows derivatographic analysis of this c a k sample obtained at the end of the duration of the phase (c). In Fig.7 grain distribution of chalk samples achieved in 6 hour of the process phase (a), in 50 hours of the process phase (b) and 20 hours of phase (c) in the continuous phase is presented.

The filtration properties of the chalk-suspension obtained in phosphogypsum conversion process are described by equation (3):

$$v^2 + 2c.v = K \cdot t \qquad \text{eq.(3)}$$

where

v - filtrate volume $[m^3]$
t - filtration time $[s]$
c - filtration coefficient describing the resistance of the filter cloth ($c=5,64 \cdot 10^{-5}\ m^3/m^2$)
K - filtration coefficient describing the precipitate and liquid properties ($K=41,89 \cdot 10^{-5}\ m^2/s$)

The filtration curve determined experimentally is presented on Fig.8.

The crystal sizes and crystal size distribution have an effect on moisture content in the filtered off soil chalk. The dependence of the moisture of the filter cake on crystal equivalent diameter determined by sedimentation method is illustated in Fig.9.

In the Fig.10 electron-microscope picture of the chalk-crystals are presented (enlargement - 1000 x - STEREOSCAN- produced by Cambridge Instrument).

AGRONOMIC PROPERTIES OF THE SOIL-CHALK PRODUCED FROM PHOSPHOGYPSUM

Soil chalk belongs to the new form of deacidifying fertilizers. The greenhouse and field studies have been completed in which soil-chalk have been evaluated agronomically. The agronomic tests proved the higher deacidifying properties in comparision with grinted mineral calcium carbonate The soil-chalk application in dose of 1 t /hec the increase pH from 4,6 to 5,6 was recorded and using the same dose of mineral chalk pH of the soil was changed from 4,6 to 5,1.The greenhouse and field studies made by Institute of Soil and Fertilization (Pukawy) stated that it is possible higher fertilization of this product even in the dose of 2 t/hec without negative influence in vegetation of the plants. The field studies indicated the increase of crop about 12% in comparison with experimental fields where soil-chalk was not used. The crystaline form of this deacifying fertilizer and phosphorous compounds, as $CaHPO_4.2H_2O$ and unreacted phosphate rock this main adventage of this product. During fertilization in the dose of 2-4 t soil-chalk/hec the additional amount of P_2O_5 is introduced to the soil (about 40-80 kg P_2O_5/hec).

The chalk filtered off on a filter press without additional operation of drying (moisture content 25-32%) was directly transported to farms in the vicinity, where, with the use of a mechanic fertilizer digging reel type-PIAST (polish production) the product was applied for deacidification of soil in the amount of 2-4 T/hec.

CONCLUSIONS

The application of the presented single-stage conversion process as an integral part of a waste-free method of processing phosphate rock ensures the obtainment of:

-full phosphogypsum utilization

-production of the soil chalk needed in acidic soils.

Pilot-plant production have shown that the chalk produced contains more than 70% $CaC0_3$ (counting the dry mass) and may be successfully used as a soil-chalk.

The application of an automatic ‘press enables the chalk obtainment with moisture content not greater than 25% suitable for direct spreading into fields with fertilizer digging reels.

In the process,a part of the P_2O_5 forms contained in phosphogypsum is recovered, because the part passes to the liquid phase in the conversion process, but a part in the form assimilable by plants, remains in the chalk, in great amount of about 50-60%.

In fertilization of 2-4 t of chalk/hec,40-60 kg P_20_5, soluble in 2% citric acid, can additionally be introduced to the soil. Pilot plant production have shown that in the single step conversion process it is possible to achieve the conversion degree of phosphogypsum to chalk in the range 92-96%.The determination of grain-spize distribution has shown that the chalk crystals are homogeneous, -though very fine, as the position of maximum grain-size density distribution is about 10-15 μm.

It should also be pointed out that the process does not cause any operating difficulties due to the air tightness of the apparatus. Ammonia losses are avoided in the process as a result of using absorption solutions in the circulation technological process.

The results of the industrial experience concerning acidulation of the phosphate ores in the presence of ammonium ion, washing phosphogypsum with sulfuric acid on a filter and fertilizer NPK 14:14:14 production, together with the the development of a new single-stage conversion process made it possible to develop a new waste-free method of processing phosphate ores.

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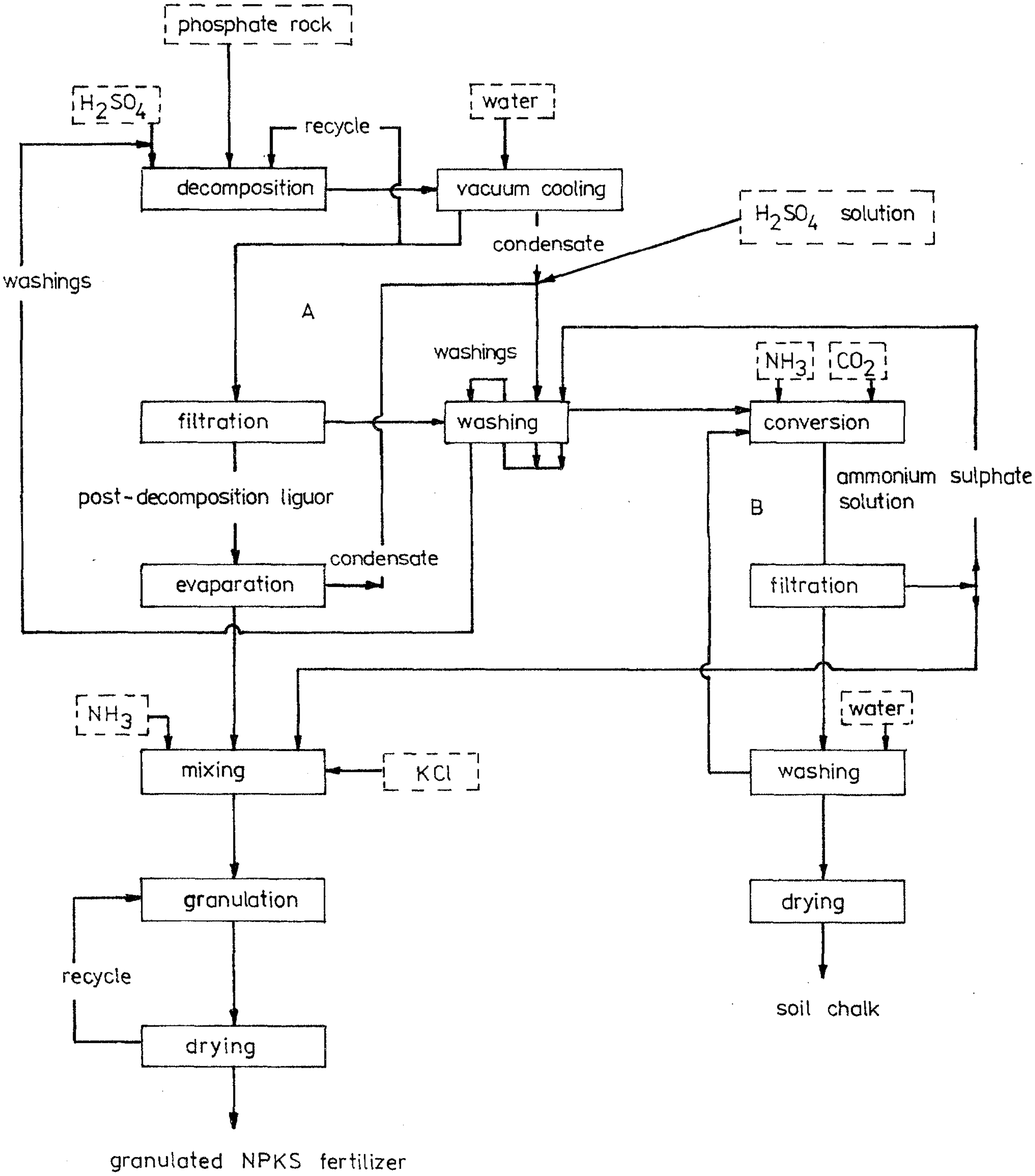


Fig. 1. Waste-free method of NPK fertilizer production and soil-chalk instead of phosphogypsum

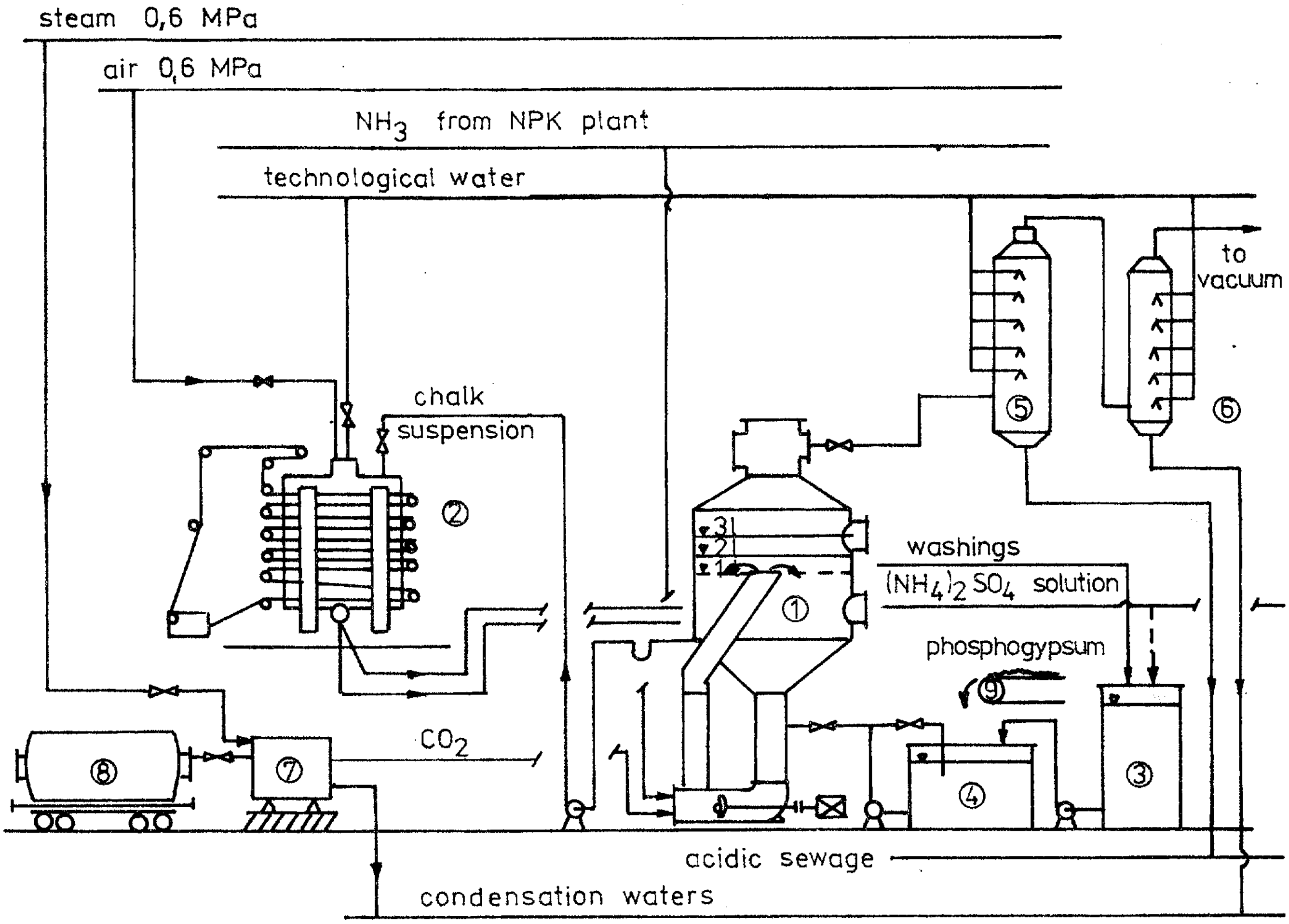


Fig. 2. Technological flow-sheet of a semi-technical pilot installation for phosphogypsum conversion :

1 / reactor - crystallizer
2 / filter - press
3 / washings tank
4 / water scrubber
5 / repulpation tank
6 / water condenser
7 / mixer
8 / liquid carbon dioxide tank

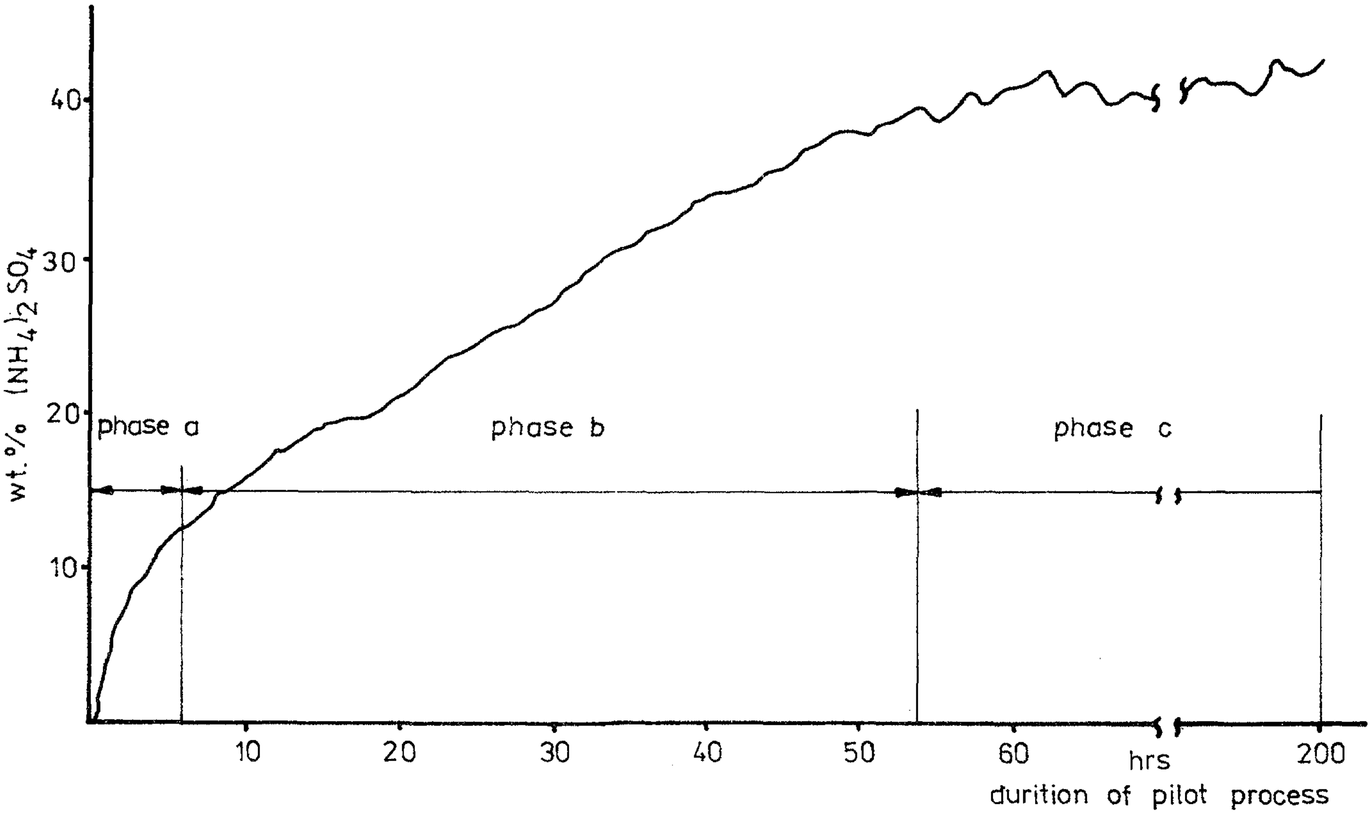


Fig. 3. Dependence of ammonium sulphate concentration in realization of the process on a semi-technical scale

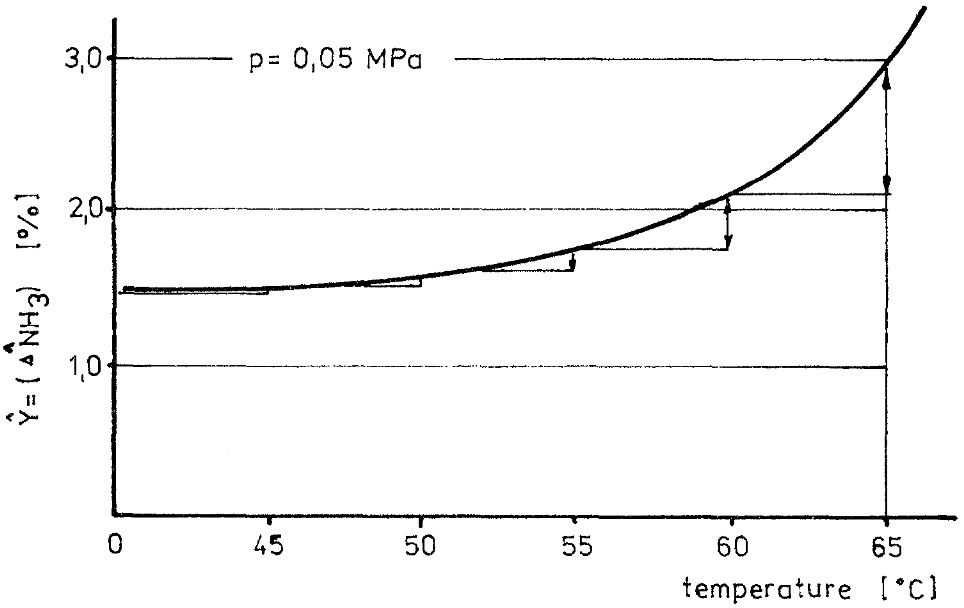


Fig. 4. Dependence of the degree of ammonia desorption from the vacuum conversion reactor (%) on temperature

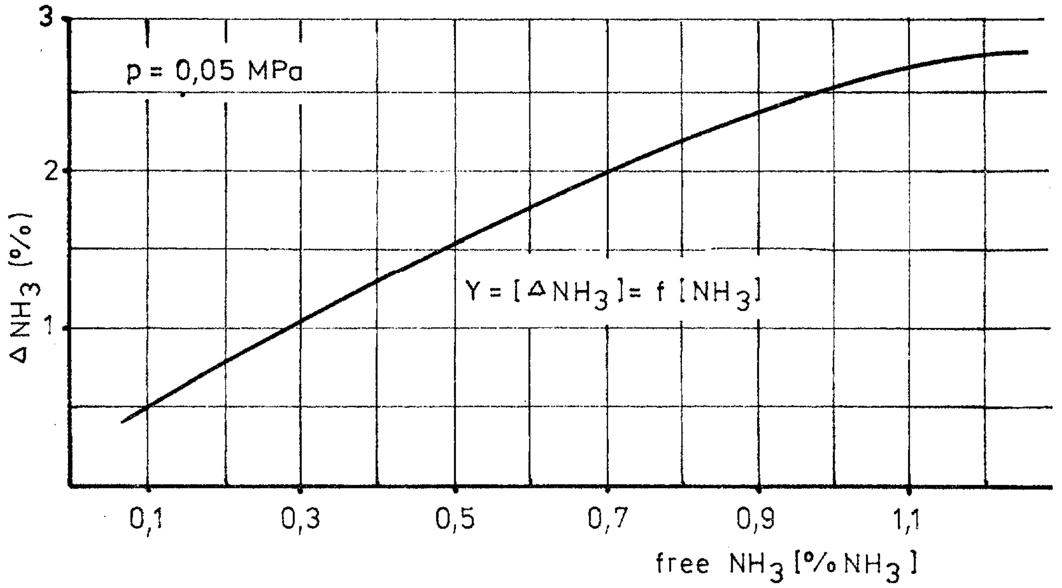
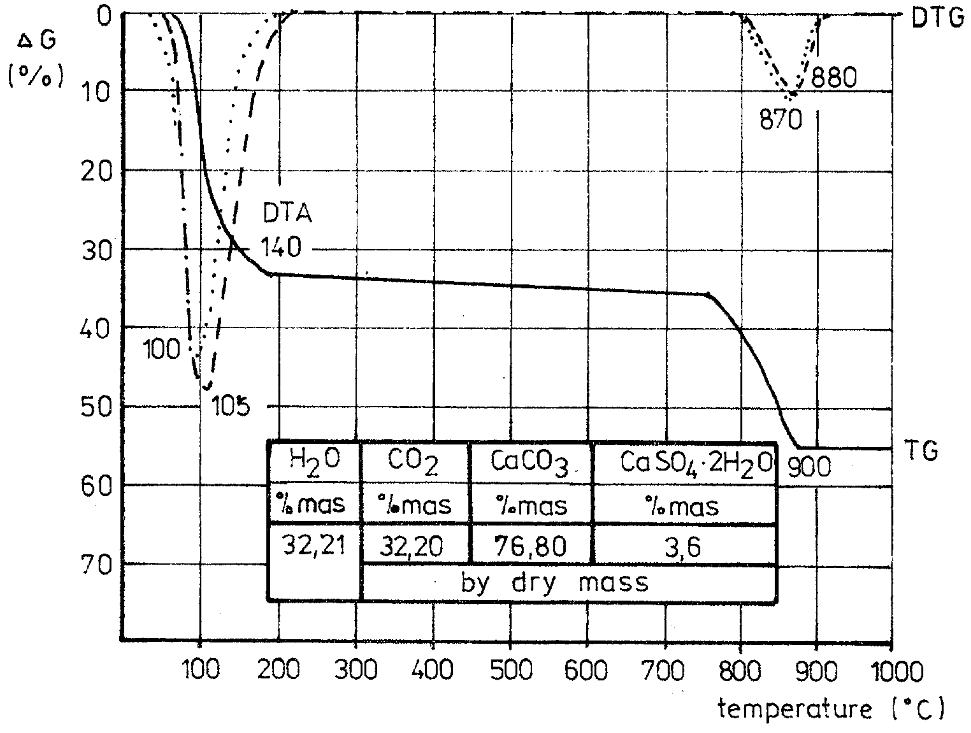


Fig. 5. Dependence of the ammonia desorption on the NH (free) concentration contained in the liquid phase in the conversion process



H_2O	CO_2	$CaCO_3$	$CaSO_4 \cdot 2H_2O$
% mas	% mas	% mas	% mas
32,21	32,20	76,80	3,6
	by dry mass		

Fig. 6. Termogravimetric analysis of soil chalk sample taken from filter press

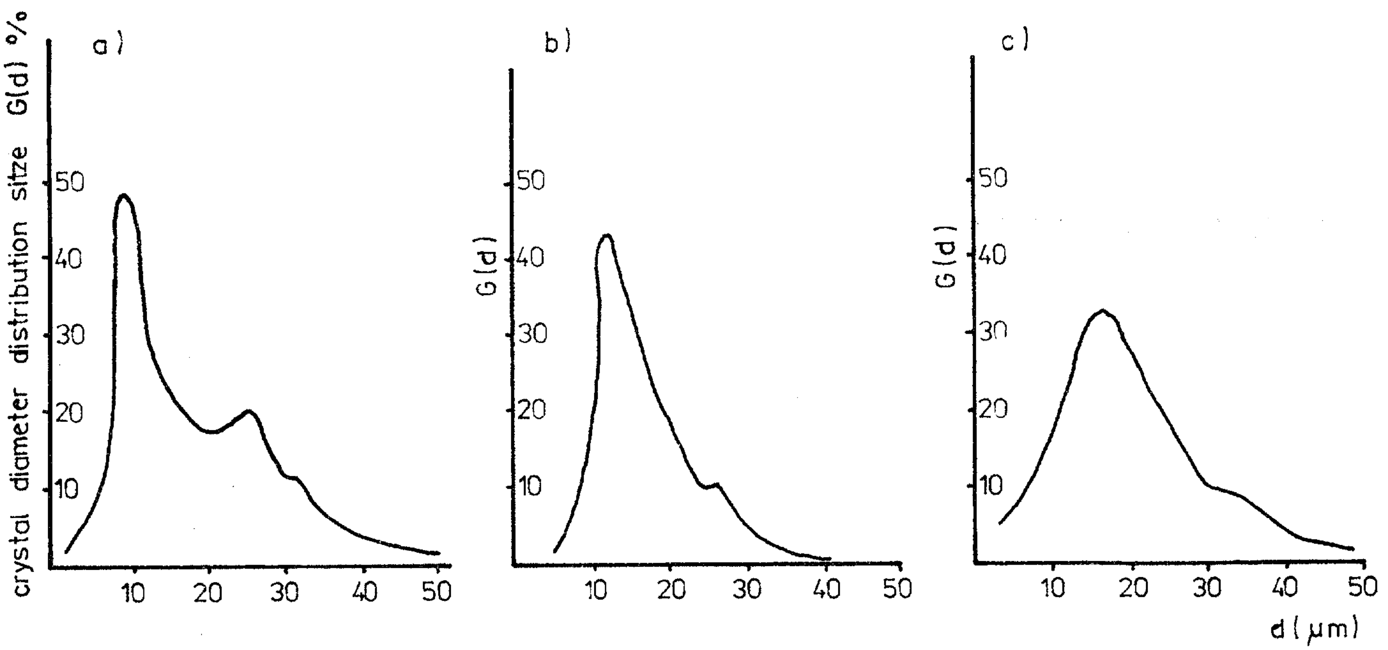


Fig.7. Grain distribution of chalk crystals obtained in the final phases (a, b, c) or the model process

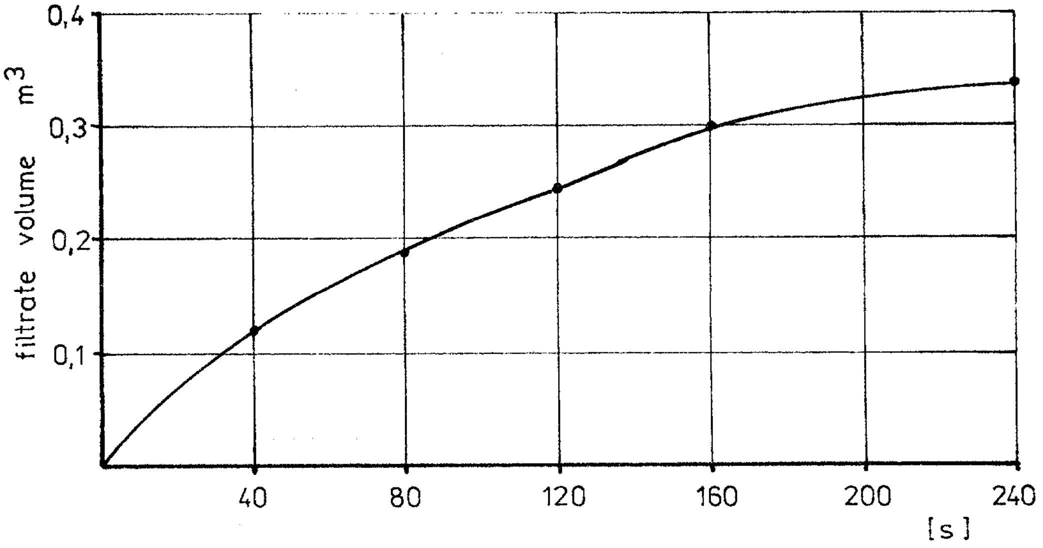
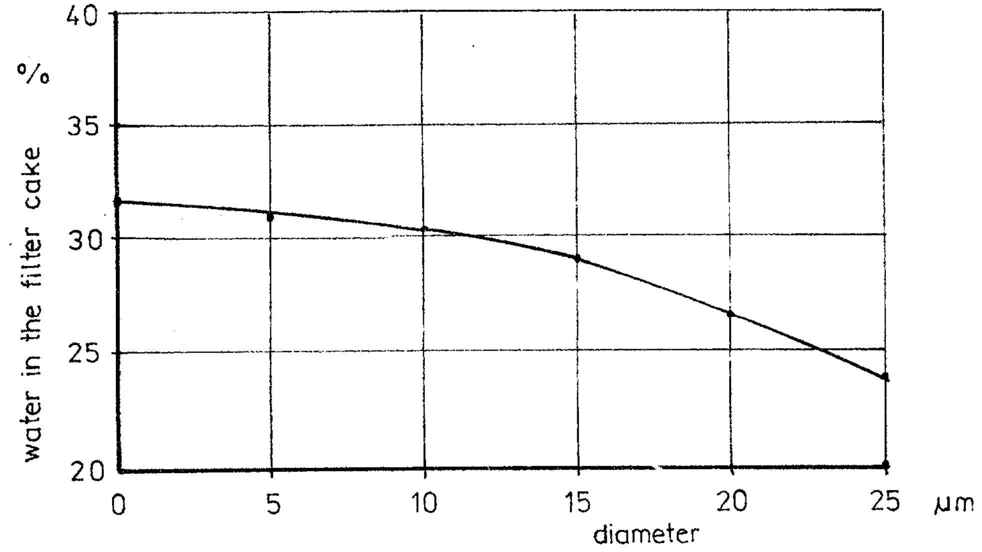


Fig. 8. Filtration curve of the soil - chalk suspension



g. 9. Dependence of water content in the filter coke on crystal size distribution as equivalent diameter

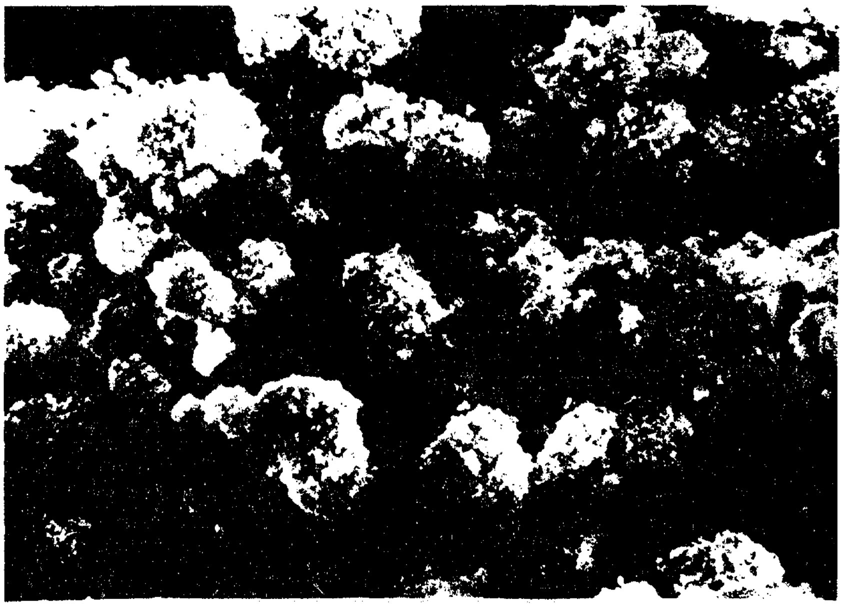


Fig. 10. Crystals of the soil chalk (enlargement 1000 x - scaning microscope)

Table 1.Operating condition for pilot-plant production of soil chalk and ammonium sulfate solution.

Parameters	Units	Phase(a) [0-6 hrs]	Phase(b) [6-54 hrs]	Phase(c) [54-100hrs
<u>Materials fed</u>	kg/h			
ammonia (p=0,2MPa)	"	68,2	146,0-152,0	138,0-177,5
carbon dioxide(")	"	86,0	184,0-190,0	181,0-232,5
phosphogypsum	"	470,0	1000	1000-1250
temperature	°C	38,0-50,0	52,0-55,0	53,0-56,0
preasure	MPa	0,06-0,07	0,05-0,055	0,05-0,055
liqiud/solid	kg/kg	4,00-7,98	3,2-3,8	3,7-4,1
<u>Concentration-in liquid</u>				
ammonium sulfate	$\%(NH_4)_2SO_4$	0-12,65	12,65-39,8	38,0-42,0
free ammonia	%N	0-1,40	1,1-1,3	0,8-1,1
free carbon oxide	$\%CO_2$	0-2,0	1,2-1,65	0,9-1,45
phosphate ion	$\%P_2O_5$	0,13-0,05	0,05-0,09	0,09-0,12
pH		3,8-9,4	8,8-9,0	8,6-8,8
<u>Conversion efficiency</u>	%	0 - 88,6	85,0-94,0	92,0-95,0

Table 2.Value of the regression coefficients of the equations $\hat{y}=\Delta\hat{NH}_3(\%)=b_o+\sum b_i x_i+\sum b_{ii} x_i^2$.

$\hat{y}$	b_o	b_1	b_{11}	b_2	b_{22}	b_3	b_4	b_5
ΔNH_3		$[t]$	$[t^2]$	$[NH_3]$	$[NH_3]^2$	$[SO_4]$	d_p	p
(%)	-0,939	-0,22	0,003	3,34	-1,073	-0,031	5,18	-21,22

R=0,694

Snedecor test
$F=10,91 > F_k=2,87$

<u>Independent variables</u>	mean value
t-temperature of reaction pulp [°C]	52,3
$[NH_3]$-free NH_3 content in liquid phase [%]	0,7
$[SO_4]$-concentration of sulfate ion [%]	39,3
p - pressure in reactor [MPa]	0,052
d_p - density of reactor pulp [Kg/dm³]	1,214

Table 3. Composition of the produced soil chalk, the utilized phosphogypsum produced from Florida Central phosphate raw material.

Components	soil chalk (after drying)	phosphogypsum (from Prayon filter)
$CaCO_3$	76,8	-
$CaSO_4 \cdot 2H_2O$	3,6	74,15
$Ca_5F(PO_4)_3$	0,9	0,49
$CaHPO_4 \cdot 2H_2O$	2,4	0,95
P_2O_5(water soluble)	0,1	0,45
$(NH_4)_2SO_4$	2,4	0,03
F	1,3	0,62
Fe	0,17	0,09
Mg	0,06	0,14
Al	0,14	0,08
Sr	0,20	0,10
Na	0,07	0,05
K	0,07	0,06
Si	3,32	1,89
H_2O	6,66	19,70
other	1,80	1,20

ON THE THERMOCHEMICAL RECOVERY OF SULPHUR FROM PHOSPHOGYPSUM

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Using isothermal, thermogravimetric and other investigations on the thermochemical decomposition of different kinds of phosphogypsum, natural and pure gypsum with solid and gaseous reducers in the temperature range of 1133-1273°K, dependences explaining the influence of the structure and the composition of the solid phase on the kinetics of the process have been deduced. In some of the cases, the kinetic parameters of the process have been determined by mathematical processing of the experimental data.

INTRODUCTION. The quantity and the quality of the waste phosphogypsum /PG/ from the production of extractive phosphoric acid /EPA/ have been determined by the type of the utilized phosphatic raw material raw material and the engineering-technological process /1,3/. Simultaneously, during the past years, the quantity of waste gypsum has rapidly increased owing to the wide-spread application of the "lime-limestone" method for purification of waste gassesfrom the thermoelectric power plants. The loss of sulphur and its accumulation as gypsum leads to ecological disbalance which calls for creation of new technologies for recovery of sulphur and reuse in different processes for its effective utilization.

The guidance of the process of thermochemical decomposition of $CaSO_4$ to CaS or CaO depends on the thermodynamic equilibrium between reactions 1,2,3, connected between each by the partial pressure of the gas components /Fig.1/:

$$CaSO_4 \rightleftharpoons CaS + 2O_2 \qquad /1/$$

$$CaSO_4 \rightleftharpoons CaO + SO_2 + 0{,}5O_2 \qquad /2/$$

$$CaO + SO_2 \rightleftharpoons CaS + 1{,}5O_2 \qquad /3/$$

Evidently, the preparation of CaS is possible at the temperature of 1100-1273°K only if the partial pressure of oxygen /PO_2/ is rather low. Usually, it can be reached by introducing of a reducing component into the system. Thus, the impurities of Fe_2O_3, Al_2O_3 and SiO_2 in gypsum and the presence of a reducer can expand the field of Ca on account of the by-reactions which take place and lead the system to the initial equilibrium:

$$CaO + SiO_2 \rightleftharpoons CaSiO_3 \qquad /4/$$

$$CaO + Fe_2O_3 \rightleftharpoons CaFe_2O_4 \qquad /5/$$

$$CaO + Al_2O_3 \rightleftharpoons CaAl_2O_4 \qquad /6/$$

$$SO_2 + 2H_2 \rightleftharpoons 0{,}5S_2 + 2H_2O \qquad /7/$$

$$0{,}5S_2 + H_2 \rightleftharpoons H_2S \qquad /8/$$

In order to eliminate the loss of sulphur at the dicomposition of gypsum to CaO and SO_2, reactions 7 and 8 should be considered. The necessity of a higher temperature appear as a disadvantage of this process. The thermochemical decomposition of gypsum to CaS is an exothermal process /Table 1/. In this way, from energetic point of view, the decomposition of gypsum to Cas is more advantageous.

$$CaSO_4 + 4H_2 \rightleftharpoons CaS + 4H_2O \qquad /9/$$

$$CaSO_4 + 4CO \rightleftharpoons CaS + 4CO_2 \qquad /10/$$

$$CaSO_4 + CO \rightleftharpoons CaO + CO_2 + SO_2 \qquad /11/$$

$$CaSO_4 + H_2 \rightleftharpoons CaO + H_2O + SO_2 \qquad /12/$$

The thermochemical decomposition of gypsum and phosphogypsum can be realized with solid as well as with gaseous reducers. Besides, the introduction of mineral impurities with the solid reducers leads to decrease of the CaS content in the solid reducer. As we have already mentioned above, some of them can lead to shift of the equilibrium and acceleration of the process /3,4/.

TABLE 1

Change of the Enthalpy /K/ for Reactions 9-12
at the Temperature of 900-1400°K

Reaction No.	900 K	1000K	1100 K	1200 K	1300 K	1400 K
9	-42,8	-49,5	-56,7	-64,4	-72,8	-81,7
10	-184,3	-187,2	-190,5	-194,5	-199,1	-204,2
11	210,2	205,1	200,5	195,5	189,1	182,2
12	245,6	239,7	234,0	222,7	220,6	212,8

Thus, depending on the chemical composition and structure of the initial gypsum, concrete investigations explaining the

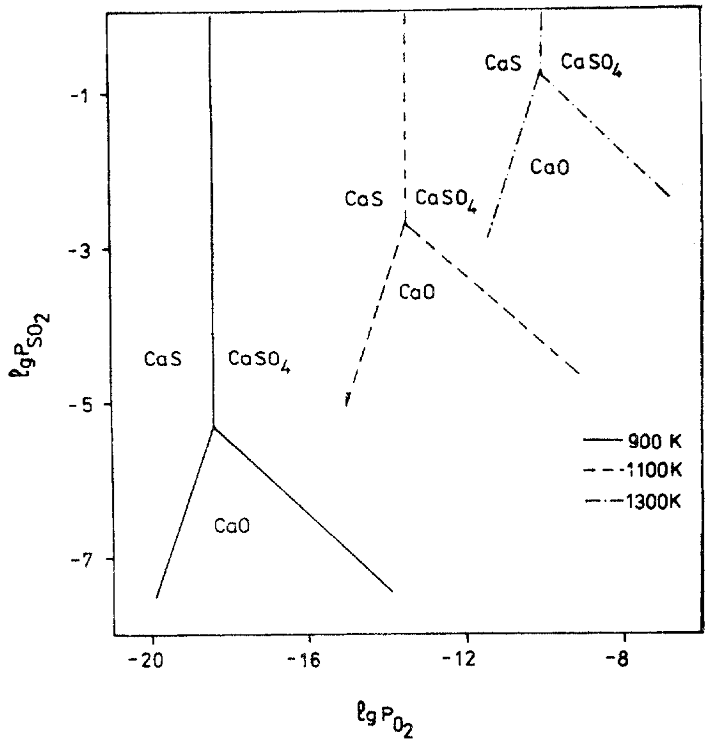


Fig.1. Kellog-diagramme of $CaO\text{-}CaSO_4\text{-}CaS$ system

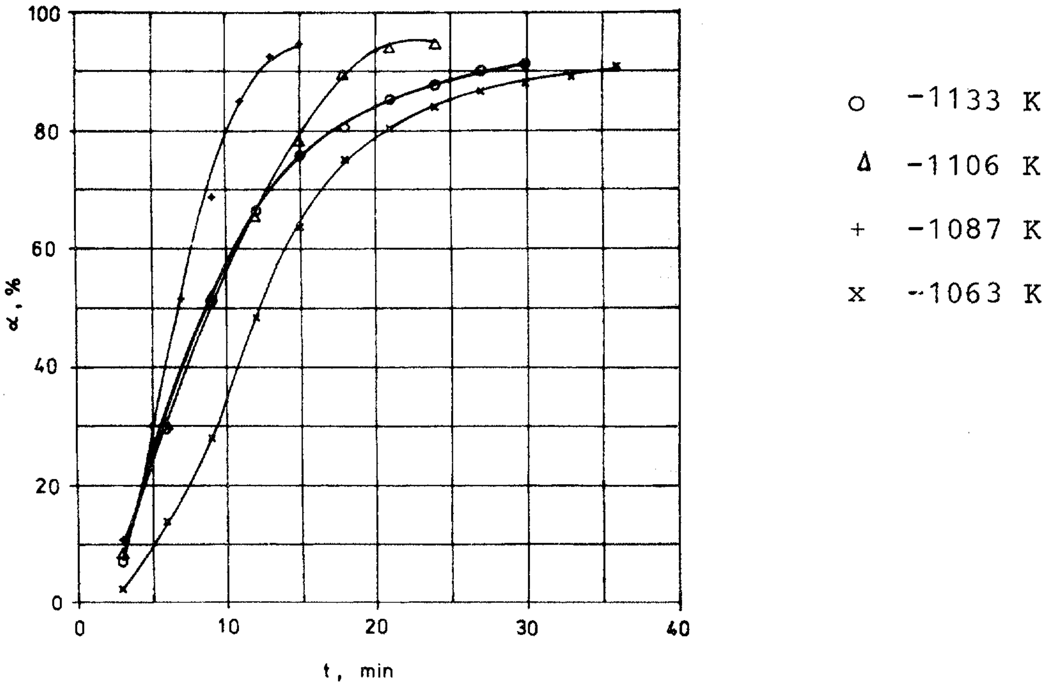


Fig.2. Dependence of α on t at $P_{H_2} = 3.10^{-3}$ Pa

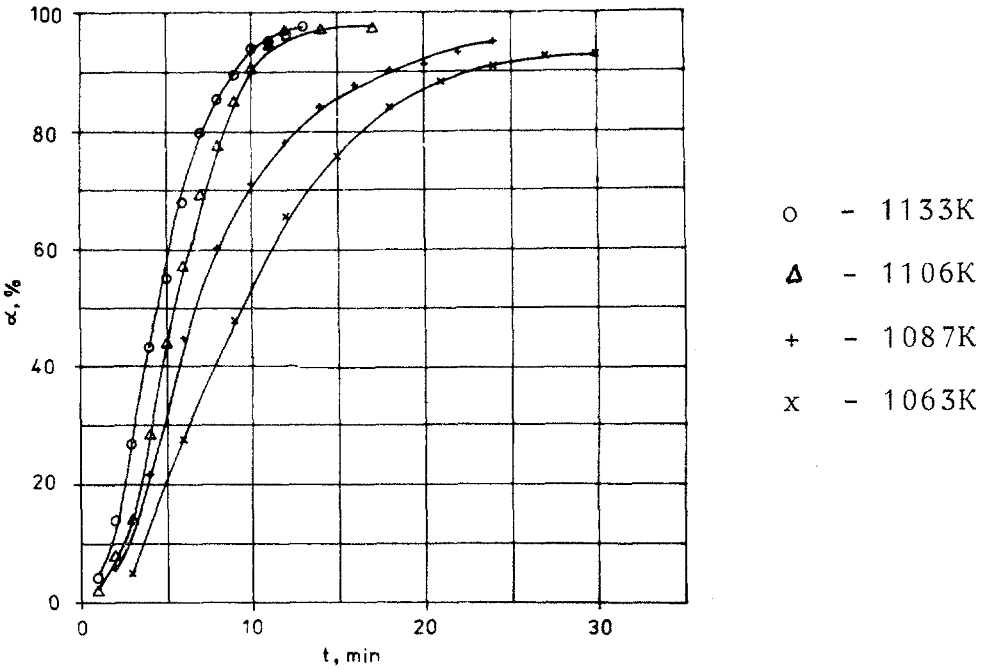


Fig.3. Dependence of α on t at $P_{H_2} = 5.10^3$ pa

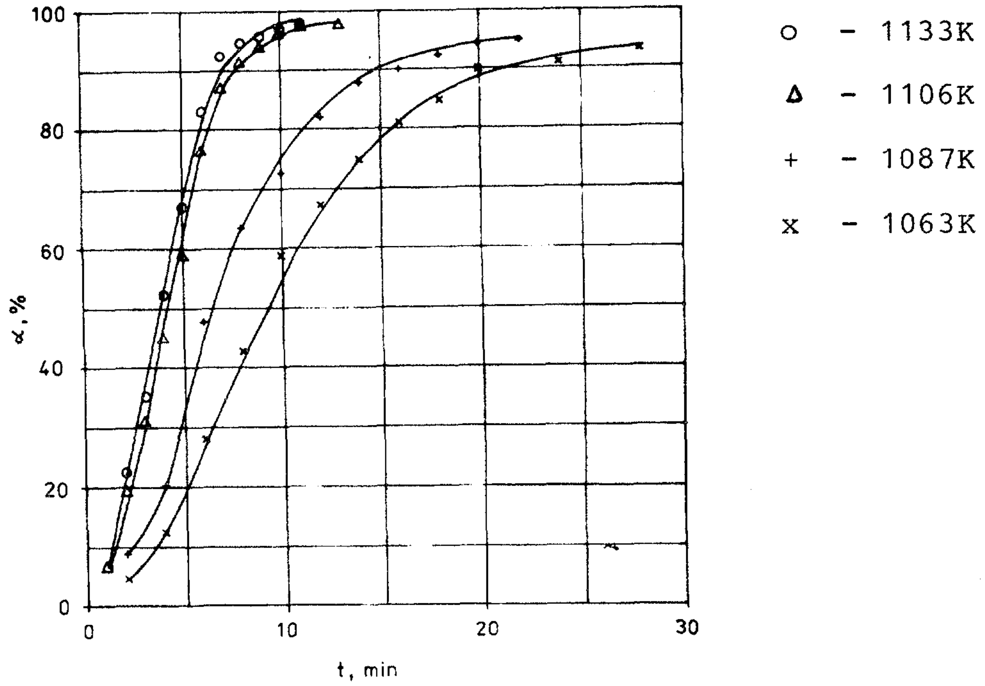


Fig.4. Dependence of α on t at $P_{H_2} = 7.10^3$ Pa

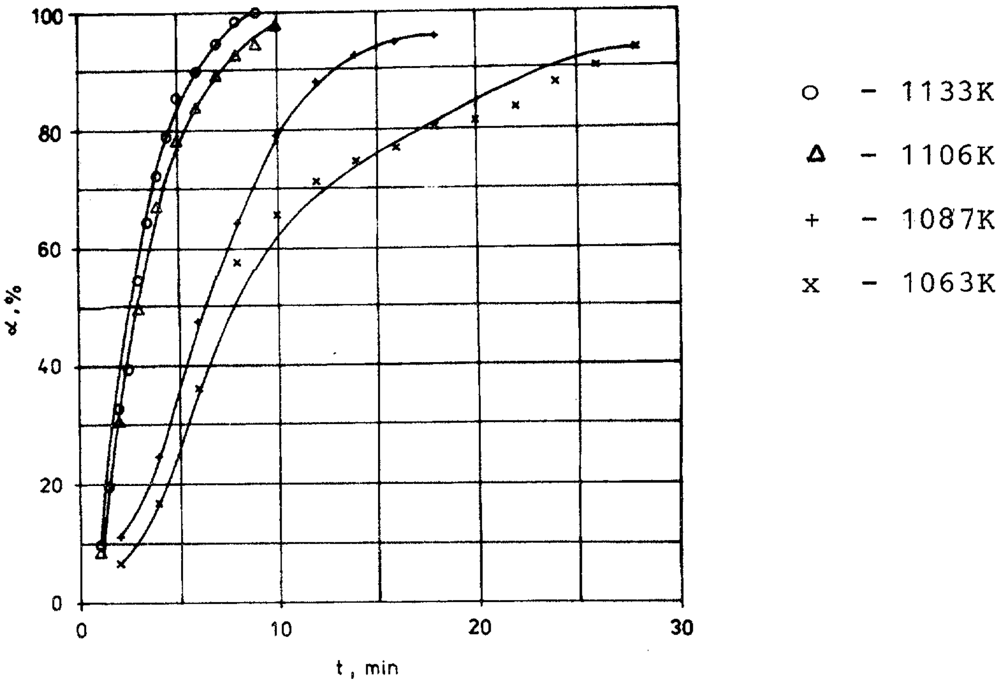


Fig.5. Dependence of α on t at P_{H_2} = 1.10^4Pa

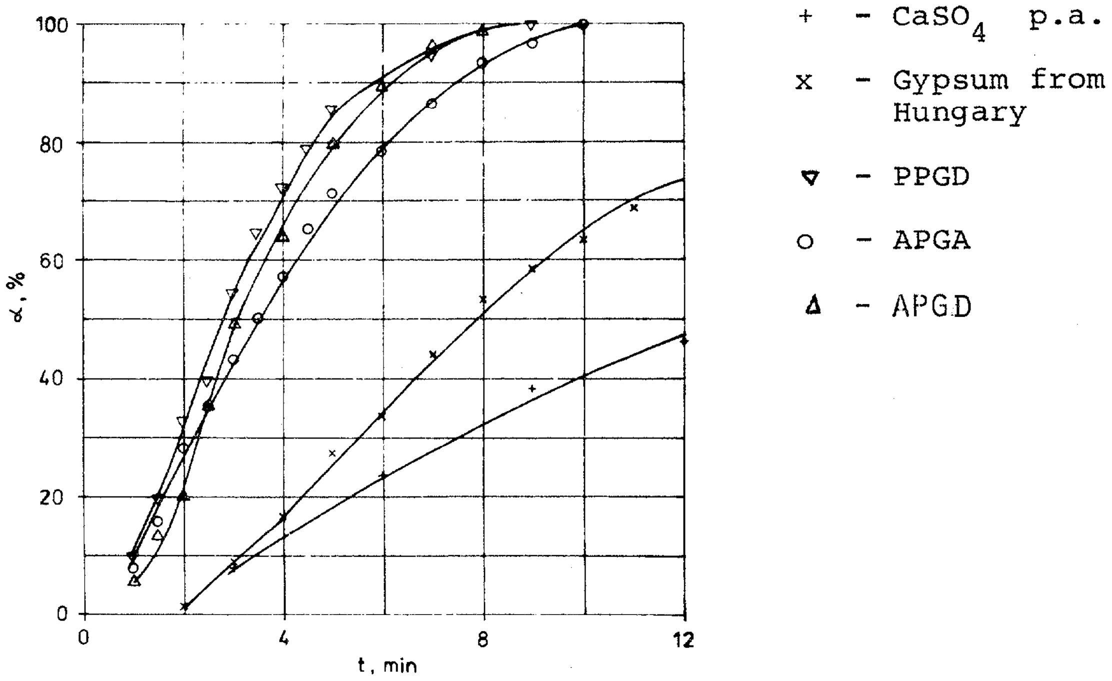


Fig.6. Dependence of α on t at P_{H_2} = $9{,}25.10^3$Pa and T=1133K

kinetic regularities of the process of decomposition have to be carried out.

The present work shows the results from the investigation on the kinetics of the thermochemical decomposition of some kinds of gypsum to CaS with different reducers.

EXPERIMENTAL. In this experiment, washed phosphorite phosphogypsum /APGD/ obtained by processing of tunisian phosphorite to EPK was used. The dry content is the following: 53,58% of SO_3; 40,3% of CaO; 0,2% of $A1_2O_3$; 0,08% of Fe_2O_3; 1,16% of the total P_2O_5; 0,09% of SiO_2 and 0,66% of impurities insoluble in hydrochloric acid: appatite phosphogypsum /APGP/ obtained by processing of hibinian appatite with the following composition: 52,48% of SO_3; 38,65% of CaO; 0,85% of $A1_2O_3$; 0,2% of Fe_2O_3; 2,83% of the total P_2O_5; 0,25% of SiO_2 and 0,65% of impurities insoluble in hydrochloric acid; appatite phosphogypsum-anhydrite /APGA/ obtained by precrystallization of APGP in sulphuric acid with the following composition: 56,08% of SO_3; 40,47% of CaO; 0,47% of Al_2O_3, 0,14% of Fe_2O_3; 0,08% of the total P_2O_5; 0,25% of SiO_2 and 0,73% of impurities insoluble in hydrochloric acid; natural gypsum /NG/ containing 51,87% of SO_3; 3959% of CaO; 0,17% of $A1_2O_3$; 1,61% of MgO; 0,2% of Fe_2O_3; 12,98% of SiO_2 and 15,42% of impurities insoluble in hydrochloric acid. Chemically pure CaSO -anhydrite is used for comparison. All of the raw material is preliminarily dehydrated at 673°K for 90 min in the presence of air. The size of the pulverized material is below 63 µm. In order to create a reducing atmosphere, gas mixtures of argon and hydrogen or carbon monoxide were used. The investigations were carried out under isothermal conditions of the thermogravimetric installation at output of the blowing gas of 27.10^{-3} m^3/h. A stand melting-pot with a diameter of 10 mm and 1 mm high was used. The weight of the initial sample is 40 mg.

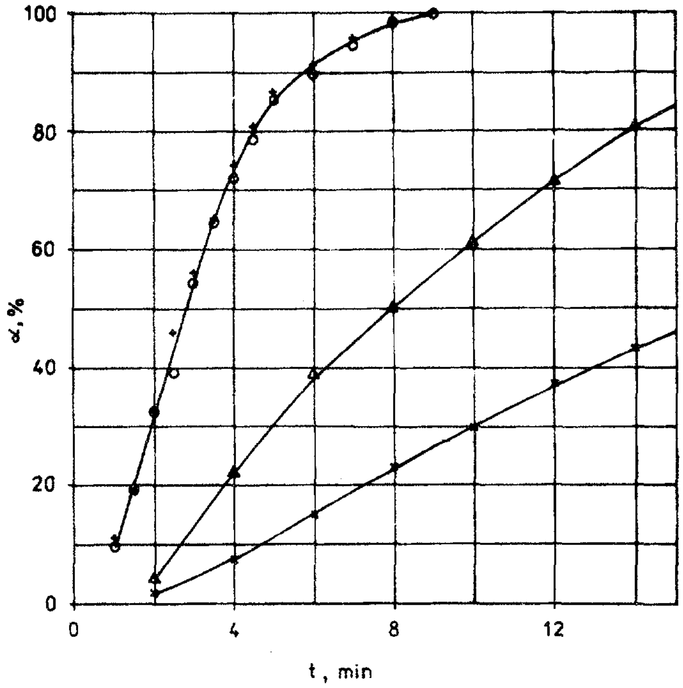
The degree of recovery $/\alpha/$ is calculated as a ratio between the losses of weight at a given moment and the maximum weight losses after the total decomposition of the sample. The content of CaS in the final product is determined iodometrically.

The dependence of the degree of decomposition of phosphogypsum /PPGD/ on the time, temperature and the partial pressure of hydrogen is given in Fig. 2-5. They illustrate the possibilities to increase the content of CaS in the final product by change of the temperature and the partial pressure of the reducer /Table 2/. At size of the particles smaller than 71 μm, temperature of 1133°K and $P_{H_2} = 10^4$ Pa, influence on the internal diffusion was not established.

The kinetic parameters of the process are determined by mathematical processing of the experimental data. The Avrami-Erofeev equation describes the reducing decomposition of phosphogypsum as follows:

$$- \ln /1 - \alpha / = /k\tau/^2$$

The obtained values of the apparent activating energy and the preexponential multiplier are presented in Table 2. The high values of the apparent activating energy well conform to the above conclusion about the insignificant influence of the diffusion transport on the kinetics of decomposition of phofphogypsum. The obtained experimental dependences /Fig. 6/



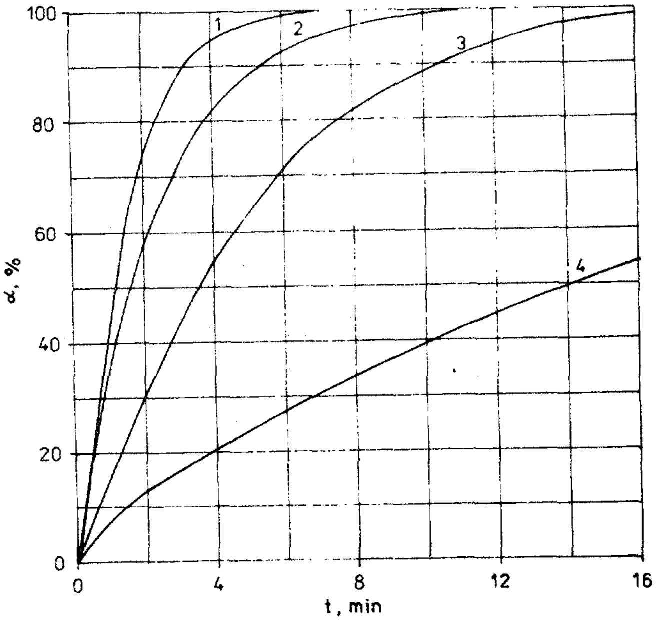
+ - $d < 63$ μ, T=1133K, $P_{H_2}=9,3.10^3$ Pa

o - $d = 63 \div 71$ μ, T= 1133K, $P_{H_2} = 9,3.10^3$ Pa

x - $d < 63$ μ, T=1133K, $P_{CO}=10^4$ Pa

Δ - $d < 63$ μ, T=1166K, $P_{CO}=10^4$ Pa

Fig.7. Dependence of α on t at different size of the particles (d)



1 - 1273 K

2 - 1248 K

3 - 1223 K

4 - 1198 K

Fig.8. Dependence of α on t for Moroccan gypsum with coals at mollal ratio of $C:CaSO_4=2,3$

Tabl.2 Experimental data and results for decomposition of diferents kinds sulphate raw materials.

Kind of raw material	T K	P atm	E kJ/mol	ln Ko	CaS %
PPGD	1063	0.029			67.50
PPGD	1087	0.029	70.8	6.57	68.91
PPGD	1106	0.029			69.32
PPGD	1133	0.029			75.08
PPGD	1063	0.049			69.23
PPGD	1087	0.049	71.3	6.81	71.23
PPGD	1106	0.049			75.12
PPGD	1133	0.049			80.03
PPGD	1063	0.069			71.44
PPGD	1087	0.069	83.0	8.15	74.18
PPGD	1106	0.069			76.28
PPGD	1133	0.069			80.11
PPGD	1063	0.093			75.66
PPGD	1087	0.093	112.4	11.41	77.87
PPGD	1106	0.093			79.54
PPGD	1133	0.093			81.49
APGD	1133	0.093			82.23
APGA	1133	0.093			90.70
Gypsum p.a	1133	0.093			96.16
Natural Gypsum	1133	0.093			59.51

confirm the significant influence of the chemical composition and the structure of the sulphate containing raw material on the kinetics of the process. The chemically pure $CaSO_4$ and natural gypsum have significantly lower reactivity compared to the various kinds of phosphogypsum.

Temperature range of 1110-1160°K and partial pressure of hydrogen appear as optimum conditions for the reducing process.

The investigations on the decomposition of phosphogypsum at the temperature of ll33°K and 1166°K in the atmosphere of 10% of CO and 90% of Ar have established the less effective reducer of hydrogen /7/.

The reduction of natural gypsum from Morocco with coal /Fig. 8/ shows that the process takes place at a higher speed in the temperature range of 1223-1273°K, i.e., with a hundred K higher than the investigations on the reduction of different kinds of phosphogypsum with hydrogen and carbon dioxide.

CONCLUSION. The carried out investigations allow us to evaluate the influence of the chemical composition and structure of the solid phase on the reactivity of sulphate-containing raw material. Evidently, insignificant content of impurities and ions leads to change of the kinetic regularities as well as to change of the thermal stability of the solid phase as it was described in our previous investigations /4/. In all the cases, the influence of the impurities should be connected with the possible by-reactions which can take place and draw the equilibrium in the direction of Ca or CaO as well as with the structure of the solid phase and its defectivity in result of the inclusion of some impurities in the crystal structure.

We should consider the formation and growth of the crystallites of the new phase, the distribution and precipitation on the solid particles of the sulphate raw material since the conditions for crystallization and growth determine the possibility of caking, local eutectics and other physicochemical processes leading to change of the limiting stage of the process of decomposition.

The optimum partial pressure of the reducing gas components, hydrogen and carbon monoxide is within the range of 0,05-0,1 kg/cm^2. The higher effectivity of hydrogen as a reducer is observed at the beginning of the process along the total boundary surface of solid-gas which results in a shorter inducing period.

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COMPLETE REMOVAL OF RADIUM FROM PHOSPHOGYPSUM

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ABSTRACT

For several years, we worked on the removal of radium from phosphogypsum in order to decrease and even to eliminate the environmental effects from phosphogypsum used in the construction industry and other industries.

We started with a simple hydrocycloning of a dilute slurry. As it was not good enough, we tried to find where the radium was located. We found radium in a calcium, strontiumn, baryum co-crystallized salt in a small ball shape which could be eliminated by hydrocycloning, and in small crystals sticking to the surface of calcium sulfate crystals which we did not know how to eliminate.

In 1986, we proposed a process which, due to an adjustment of the chemical equilibrium during the chemical reaction of phosphate in phosphoric acid plant, could isolate most of the Radium into a product which can be efficiently separated by hydrocycloning.

In 1989 we made another advance, which is a new process for which we asked for a patent. With this new approach we can obtain purified gypsum or phosphogypsum of a better quality, free of radium and other non soluble impurities, for special use, for instance, as a white filler.

In this new process, we calcine the raw phosphogypsum into hemihydrate and dissolve the hemihydrate in water with a water/hemihydrate ratio superior to 100 : 1. Very quickly we filter the solution. On the filter surface we collect unattacked phosphate, phosphate rock impurities and the two types of radium salts described before. The filtrate is a purified solution of calcium sulfate which crystallizes into gypsum due to the difference of solubility of hemihydrate and gypsum in water. This difference can reach 7 kg/m^3 of solution. When the crystallization is completed, the solution can be filtered through a standard filter. The cake of purified gypsum is collected as a standard phosphogypsum. The filtrate, free of radium but still containing 2 kg of calcium sulfate per cubic meter in solution, is recycled.

The radium content of the purified phosphogypsum is too small to be determined by standard test. All the radium is in the cake of the first filter. The radioactivity of the cake depends on the amount of unattacked phosphate and phosphate rock impurities collected on the filter. It also depends on the type of phosphate rock used. It can varies from 100 to 450 pCi/gram.

This product can be transported with the necessary care, to where it comes from : the phosphate mine, and stored according to regulation.

LIST OF SYMBOLS

Ca SO4 - 2 H2O Gypsum : dihydrated calcium sulfate

Ca SO4 - 1/2H2O (α or β) Hemihydrate : hemihydrated calcium sulfate

Ca SO4 (I or II) Anhydrite : anhydrated calcium sulfate

INTRODUCTION

During the first International Symposium on Phosphogypsum, we described a way to remove a part of radium from phosphogypsum by hydrocycloning treatment. However we found it difficult to decrease α emission of treated phosphogypsum below 13 pCi/gram (Fig. I) and impossible below 7 pCi/gram.

We tried to locate the remaining radium. This was the subject we developed for the second International Symposium on Phosphogypsum. We proposed a chemical process. By addition of strontium sulfate which is known as a very strong radium "extractor" and of baryum salt, it was possible to capture most of the radium into a calcium, strontium, baryum, radium co-crystallized salt in a small ball shape which can be eliminated by hydrocycloning treatment (Fig. II).

We are able to visualize the remaining radium as a deposit of very small particles (1 to 3 pm) stuck to the surface of calcium sulfate crystals. It was possible to see them with a Scanning Electronic Microscope'(Fig. III). This gave us the idea to solubilized all the calcium sulfate, to collect the small particles by filtration, and to recrystallize the dissolved calcium sulfate, free of radium.

BASIC PRINCIPLE OF THE USED PROCESS

We call :

- gypsum the dihydrated calcium sulfate Ca SO4 - 2H2O
- hemihydrate β the stucco calcined in the air : Ca SO4 - 1/2 H2O
- hemihydrate α the stucco calcined in hot water under pressure : Ca SO4 - 1/2 H2O
- anhydrite the calcium sulfate without combined water : Ca SO4.

If you put gypsum in water at 40°C you dissolve 2.8 grams of gypsum per liter of water (Fig. IV). The non soluble impurities, as the salts containing the radium, can be collected by precipitation, filtration or by centrifuge. The purified filtrate still contains 2.8 grams of gypsum per liter. If you cool this filtrate down to 0°C, the solubility of gypsum will go down to 2.3 grams of gypsum per liter. So, 0.5 grams of gypsum will precipitate in form of needles or flakes. If you filter the liquid you will collect 0.5 grams of purified gypsum as a cake and the filtrate will contain 2.5 grams of gypsum.

If you heat this filtrate up to 40°C you can dissolve another 0.5 grams of raw gypsum and start a new cycle.

A proposed industrial cycle is shown in fig. VI. In this cycle you would need a large quantity of water : 2000 m^3 per metric ton of purified gypsum. But the main part of the water can be recycled. The water loss to be compensated is due to the moisture in the removed impurities and the purified gypsum.

The big problem is the fact that we have to heat and cool the water at each cycle. The expense can be minimized by using a heat exchanger or heat pump, but there is a risk of gypsum deposit in the cooling exchanger if the cooler is not properly engineered.

If, instead of gypsum, we work with anhydrite we can use a similar cycle but with a better efficiency.

For instance we can dissolve 3.8 grams of anhydrate per liter at O°C (Fig. IV). If we heat the liquid at 40°C, the solubility is down to 2.8 grams of anhydrite per liter. We have precipitate 1.6 grams of Ca SO4 as 2 grams of gypsum, the stable phase in this condition. With such a cycle only 500 m^3 of water per metric ton of purified gypsum are necessary. But, if the calcium sulfate is not available as an anhydrite, you have to calcine your by product into anhydrite which is costly.

To be obliged to heat and cool large quantities of water is a big constraint.

If we keep a constant water temperature in the process : 20°C for instance, and dissolve anhydrite, we can only collect 0.7 grams of purified anhydrite per liter by precipitation of 0.9 grams of gypsum instead of 2 grams in the previous example. With such a cycle we need 1100 m3 of water per metric ton of purified gypsum are necessary.

IMPROVED APPROACH

A better solution is to work with hemihydrate β. You have to calcine your by-product gypsum into an hemihydrate β at 160°C. This is the industrial way used by the gypsum wallboard industry for producing hemihydrate. Then you can dissolve 9.4 grams of hemihydrate (8.6 grams of Ca SO4) per liter of water at 20°C. By hydration of hemihydrate you will be able to precipitate 8.2 grams of purified gypsum. With this cycle we need 120 m^3 of water per metric ton of purified gypsum. This is more economical than with the previous approaches.

INDUSTRIAL PROCESS

The industrial process has been developed in order to obtain very pure and white gypsum.

This process can be described as follows (Fig. VII).

- we calcine finely ground gypsum (92 % passing 100 mesh) or phosphogyspum into β hemihydrate in calcining equipment : flash calcination, kettle or other processes usually used by the gypsum wallboard industry.

- we add the β hemihydrate into a tank equipped with an agitator full of water at 30°C saturated with gypsum (2.6 grams of gypsum per liter). We can dissolve easily 5.57 grams of β hemihydrate (4.66 grams of Ca SO4 per liter of ater saturated with gypsum, for instance by using a 90 % pure β hemihydrate), in less than 1 minute.

- we add some crystallization retarding agent (protein or citric acid for example).

- then we filter the solution through a filter medium with diatomite. 99 % of the non soluble impurities, including radium salts, are retained by the filter as a cake. For instance, we obtain 0.52 grams of dry cake with a 90 % pure hemihydrate.

- the filtrate is sent to a tank into which we add gypsum germs (finely ground gypsum for instance, 90 % passing 325 mesh). Ca SO4 in solution precipitates into gypsum until we reach the maximum solubility of 2.5 grams of gypsum per liter. We obtain in ten to fifteen minutes the precipitation of 5.9 grams of gypsum crystals.

- we filter the solution in order to collect the 5.9 grams of gypsum on a filter medium and send the saturated solution back to the first tank. We collect the purified gypsum as a cake.

In our example we have the following material balance.

We started with 6.445 grams of gypsum with 91,5 % purity (0.55 grams of non soluble impurities).

After calcination we have 5.5 grams of β hemihydrate with 0.55 grams of non soluble impurities.

We retained 0.52 grams of non soluble impurities as a cake on the first filter.

On the second filter we retained 5.895 grams of gypsum plus 0.03 grams of impurities, a total of 5.925 grams of gypsum with a 99.5 purity.

We needed 0.925 grams of water in order to hydrate our β hemihydrate into gypsum. We had to add this amount of fresh water into the first tank plus the amount of moisture in the cake of impurities and of purified gypsum. The total amount of water to be added into the first tank can reach 5.22 grams, if the impurities and gypsum cakes containing 40 % water on wet basis after filtration.

In summary (fig.VIII) to obtain 1 unit of purified dry gypsum from a 91.5% pure gypsum we have to calcine 1.088 unit of raw gypsum, to add 0.88 unit of fresh water. Then we have to dispose of 0.087 unit of dry impurities or 0.145 unit of wet impurities with a 40 % water content on wet basis.

The total amount of water to be recycled is 168.8 units.

If you want to produce 1 metric ton of purified gypsum per hour, you need a tank capacity of 45 cubic meters for dissolving and crystallization of calcium sulfate and 0.88 cubic meter per hour of fresh water.

EFFICIENCY OF THE PROPOSED PROCESS AS A RADIUM REMOVER

Here is another typical example of the proposed process.

In this new case we treated hemihydrated calcium sulfate obtained by calcination of phosphogypsum produced by a NISSAN plant. This hemihydrate was placed in an aqueous phase kept agitated and at a temperature of 15°C. The aqueous solution contained 8.4 grams per liter of calcium sulfate (expressed in dissolved calcium sulfate). The pH was adjusted to 7.

At the end of the dissolution operation, the aqueous solution of calcium sulfate was separated by filtration from the solid insoluble phase formed by the existing impurities which were to be removed.

The aqueous solutions separated in this manner was seeded by means of a ground gypsum germs (approximately 1.3 grams per liter) in order to initiate the recrystallization of the purified gypsum. We obtained approximately 6.9 grams per liter at the end of one hour.

The level of radioactive contamination was measured using a BERTHOLD counter equipped with a HARSHAW Model 101 analysis chamber and a DJ 490 detector with a silicon semi-conductor (sold by BERTHOLD, France), on the raw phosphogypsum, the corresponding hemihydrate, the recrystallized gypsum and on the impurities separated by filtration. All the results of the radiation level expressed in Picocuries per gram (pCi/g) are assembled in the following table.

SAMPLE	LEVEL OF RADIOCATIVE CONTAMINATION RADIATION IN pCi/g	
	TOTAL	ALPHA RADIUM
Phosphogypsum	98	21
Phosphoplaster	100	29
Dihydrated calcium sulfate recrystallized in accordance with the invention	5	0
Impurities removed by filtration	315	60

Thus, the process provides purified gypsum, in which the amount of radioactive contamination has been lowered, on the order of 20 times, with a non measurable α radium radiation.

The residual 5 pCi/g may come from K 40. As potassium salts are soluble, they cannot be eliminated by our process.

ESTIMATION OF COST OF PURIFICATION

To dry the raw phosphogypsum, to calcine it, to purify it, and to dry the purified gypsum may cost a little less than 90 US $ per short ton with the European cost of energy (24 US $/barrel of bunker C fuel oil). It should drop down close to 70 US $ with US price of fuel oil.

If the phosphoric acidplant uses a hemihydrate process (PRAYON, NISSAN GARRETT or other (Fig IX)), you can directly purify the by product and save the necessary energy for drying and calcining of the raw phosphogypsum. In spite of a slightly lower efficiency of the process with α hemihydrate (see fig. IV), it is possible to save at least 20 US $ /short ton of dried purified gypsum.

DISPOSAL OF REJECTS

The radioactivity of phosphogypsum depends on the type of phosphate rock used as a raw material by the phosphoric acid plant. With some phosphate rocks, the α radium emission of phosphogypsum can reach 30 PCi/gram. Then the total emission from the impurities removed by filtration can go up to 450 pCi/gram. The problem is to dispose of this waste.

We have to face this type of problem each time we extract a component by chemical reaction from a quarried mineral. Each time, we have a concentration of impurities. The proposed way is to send the harmful impurities back to the quarry or the mine from where they have been extracted in order to go back to previous natural equilibrium.

Transportation should not be a problem as other natural products communly used as aggregates show a higher total emission than our waste material.

If necessary a dilution can be done.

The dumping area has to be treated in order to avoid any drainage by possible circulating water and the dump has to be covered by serveral feet of inert material in order to prevent radiation to reach the surface.

This purification process is under patent (application of patent has been done in France (n° 8906704), and in many other countries including U.S.) A subsidiary of LAFARGE COPPEE will use it for the purification of gypsum rock in order to produce special fillers. A pilot plant is presently in operation.

ACKNOWLEDGEMENTS

We have to thank for their help A. PETIT and his crew at the LAFARGE COPPEE RECHERCHE research center.

Hydrocycloning of slurry

Gypsum	Florida rock		Morocco rock	
	total	226 Ra	total	226 Ra
Phosphate rock	122	30	122	30
Phosphogypsum : under 160 μm	63	—	102	—
After 1st treatment : over flow	174	—	239	—
under flow	72	—	80	—
After 2nd treatment : over flow	111	—	185	—
under flow	62	13	64	13
After 3rd treatment : over flow	—	—	—	—
under flow	—	—	48	8

fig I

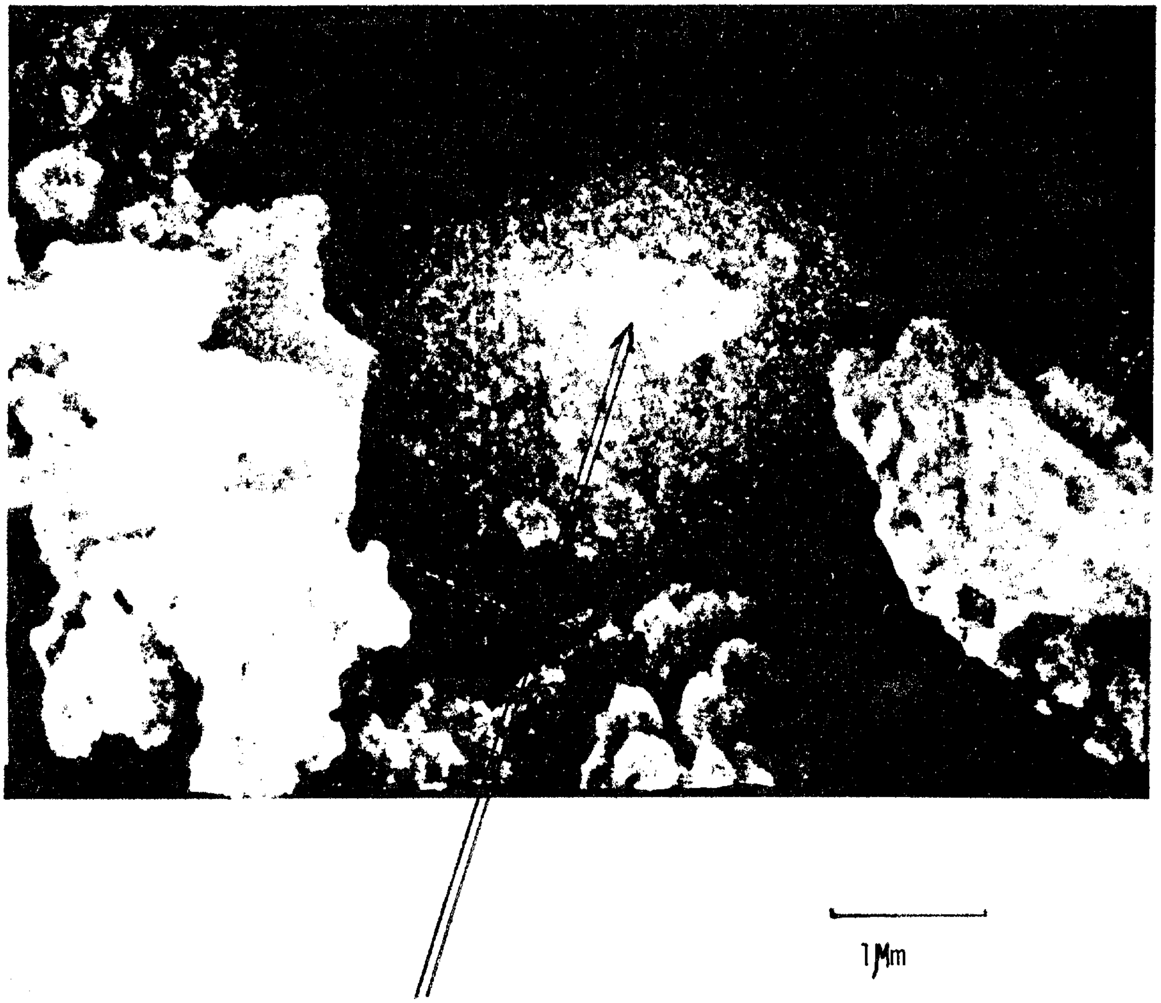


Fig. II

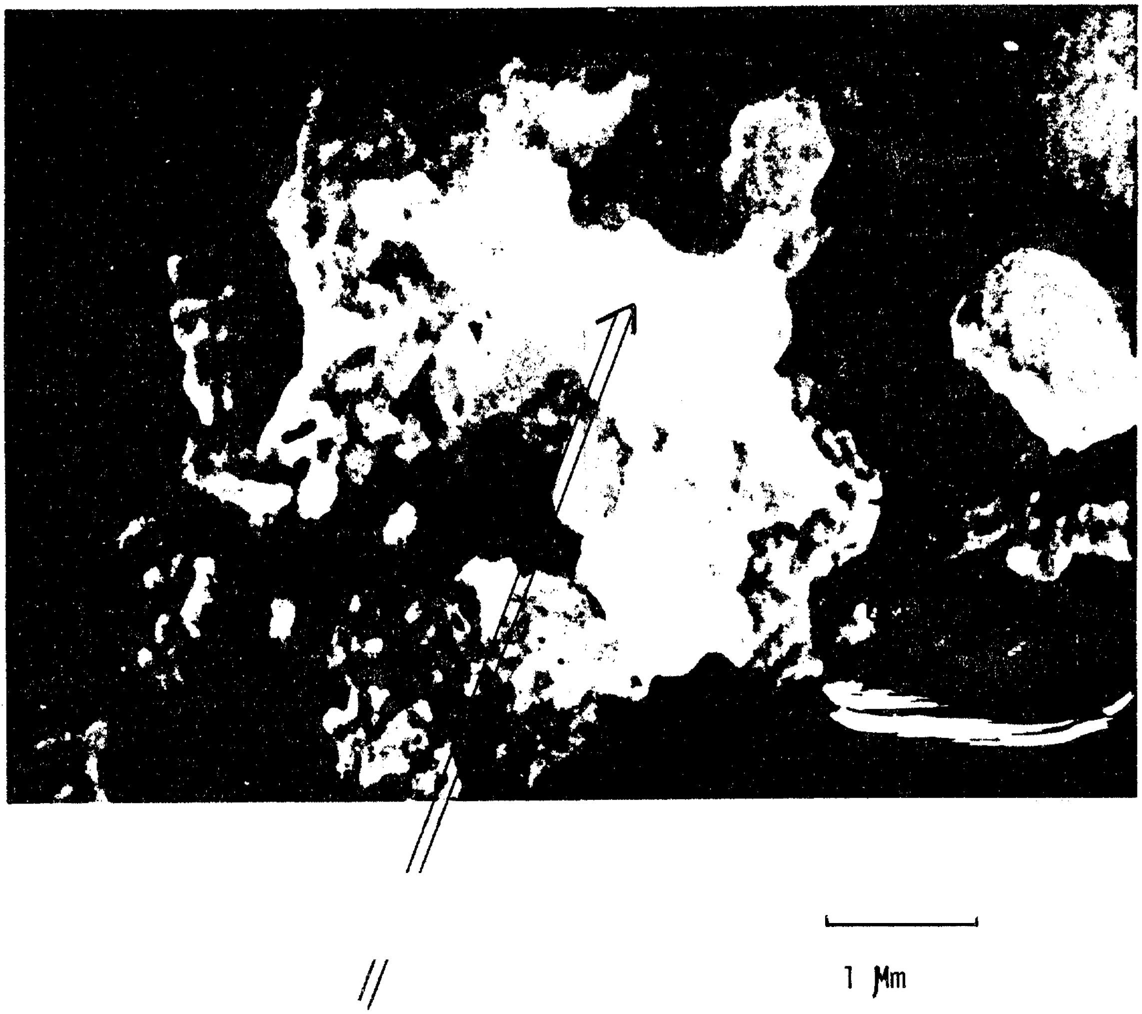


Fig. III

-Calcium sulfates solubilities-

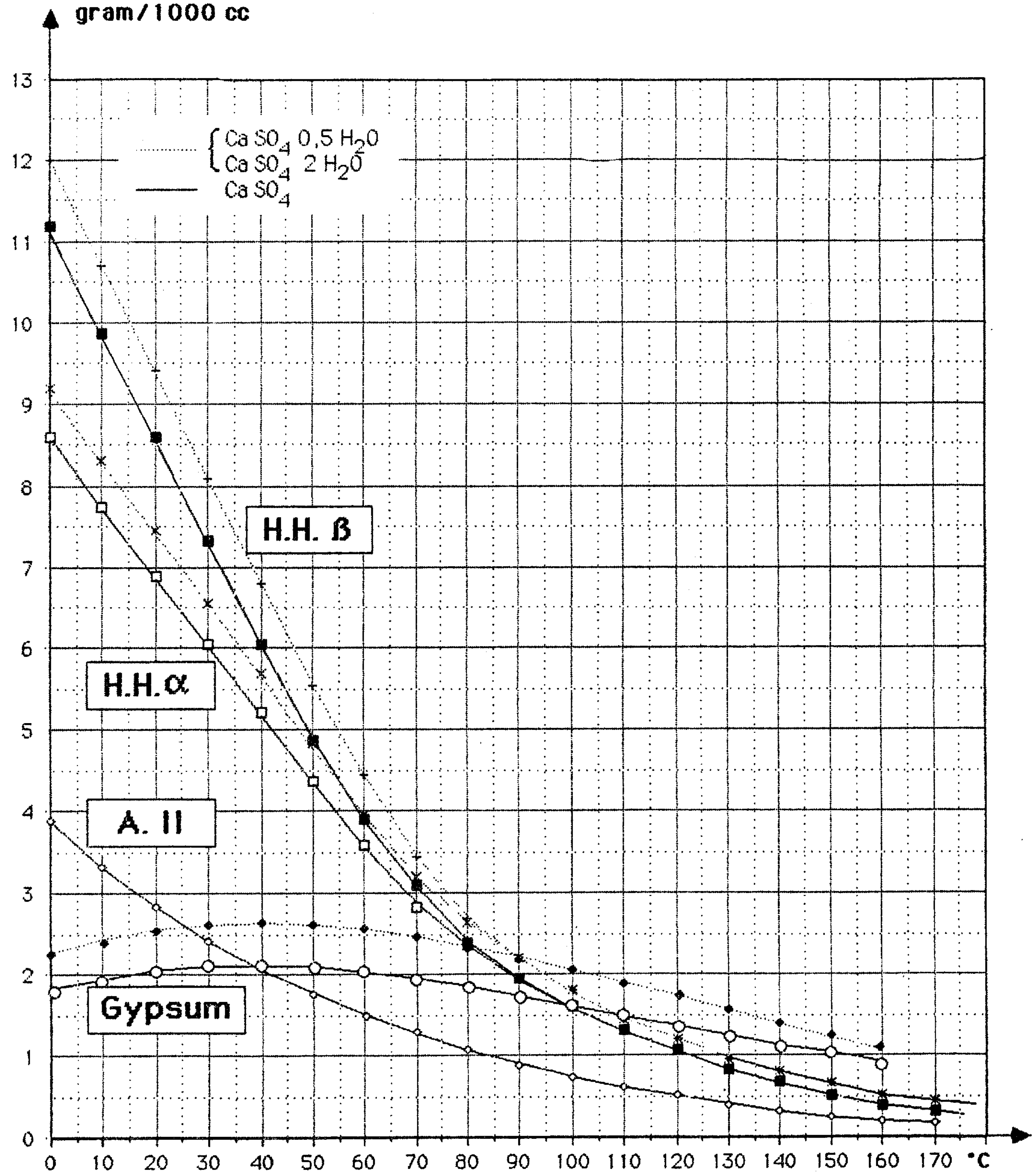
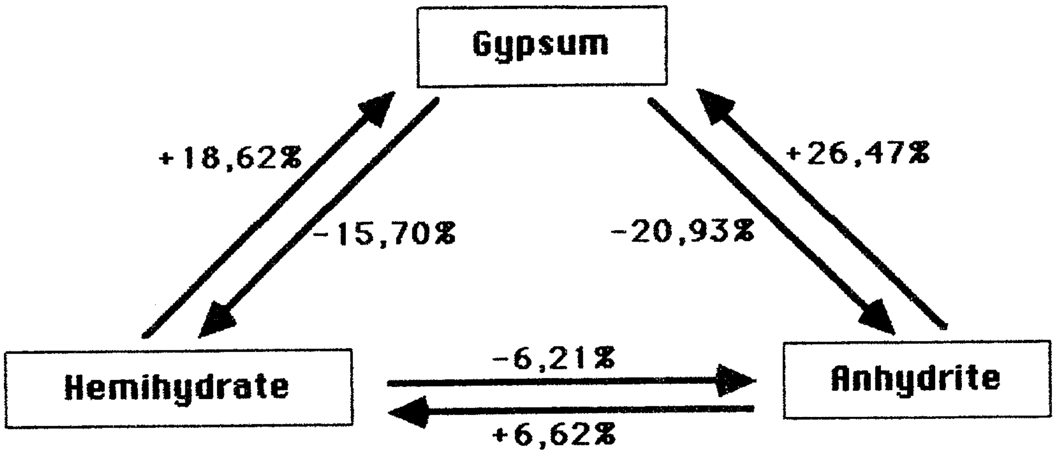


Figure IV

-Weights of calcium sulfate composites-



Note : Moleculaire weights : $CaSO_4 2H_2O$: 172,17 $CaSO_4 0{,}5H_2O$: 145,15

$CaSO_4$: 136,14 SO_3 : 80,06 H_2O : 18,02

Figure V

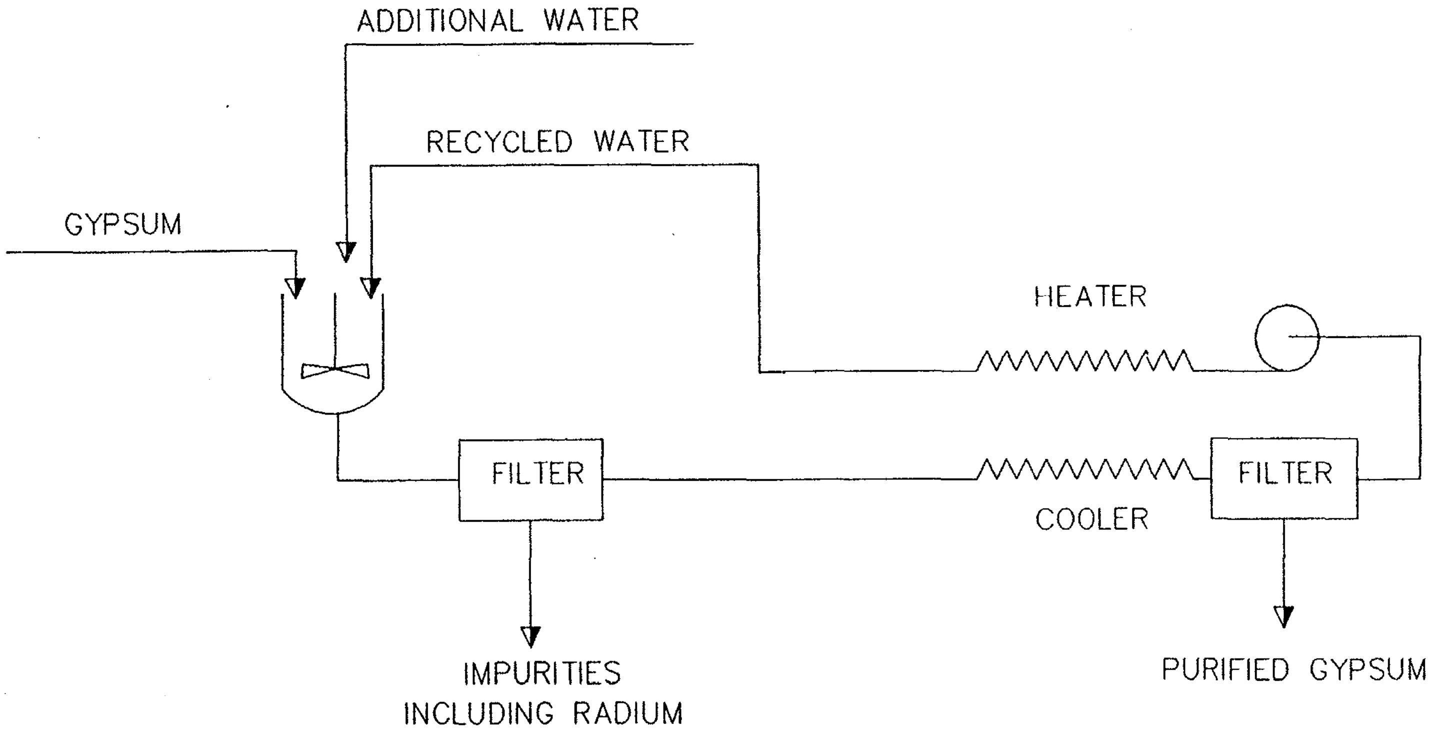

ADDITIONAL WATER
RECYCLED WATER
GYPSUM
HEATER
FILTER
COOLER
FILTER
IMPURITIES INCLUDING RADIUM
PURIFIED GYPSUM

Fig. VI

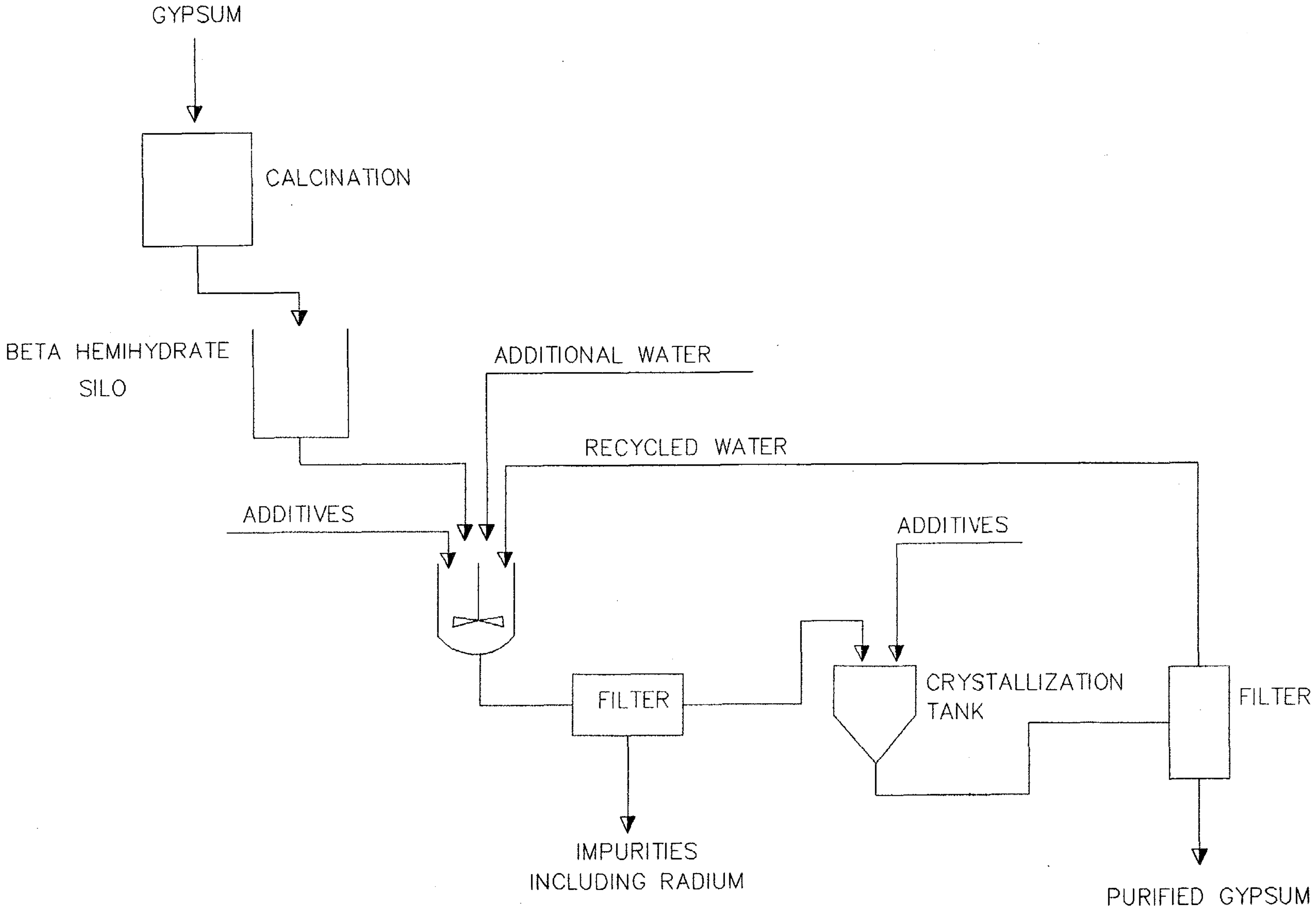

GYPSUM
CALCINATION
BETA HEMIHYDRATE SILO
ADDITIONAL WATER
RECYCLED WATER
ADDITIVES
ADDITIVES
FILTER
CRYSTALLIZATION TANK
FILTER
IMPURITIES INCLUDING RADIUM
PURIFIED GYPSUM

Fig. VII

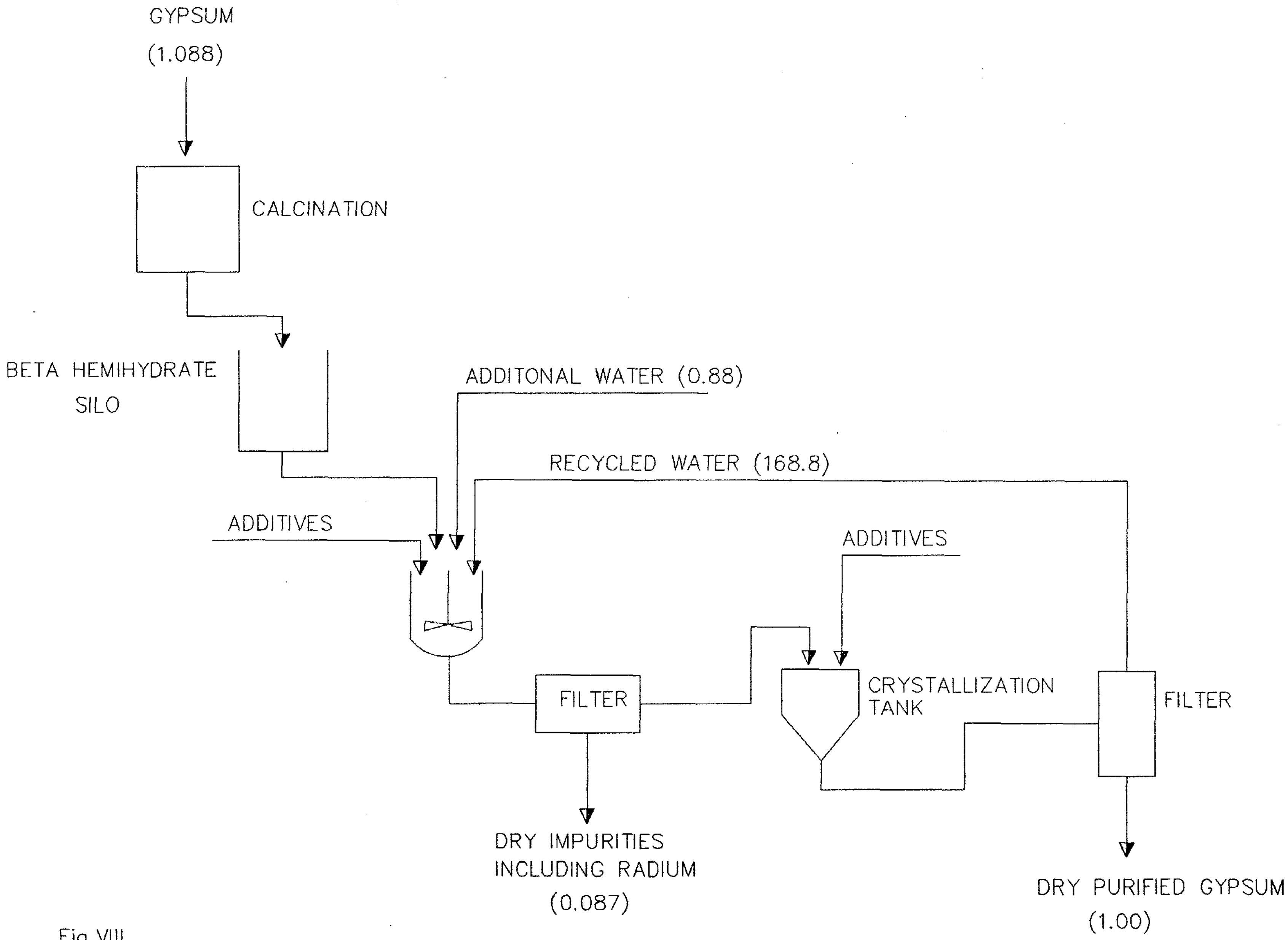

GYPSUM
(1.088)
CALCINATION
BETA HEMIHYDRATE
SILO
ADDITONAL WATER (0.88)
RECYCLED WATER (168.8)
ADDITIVES
ADDITIVES
FILTER
CRYSTALLIZATION
TANK
FILTER
DRY IMPURITIES
INCLUDING RADIUM
(0.087)
DRY PURIFIED GYPSUM
(1.00)

Fig. VIII

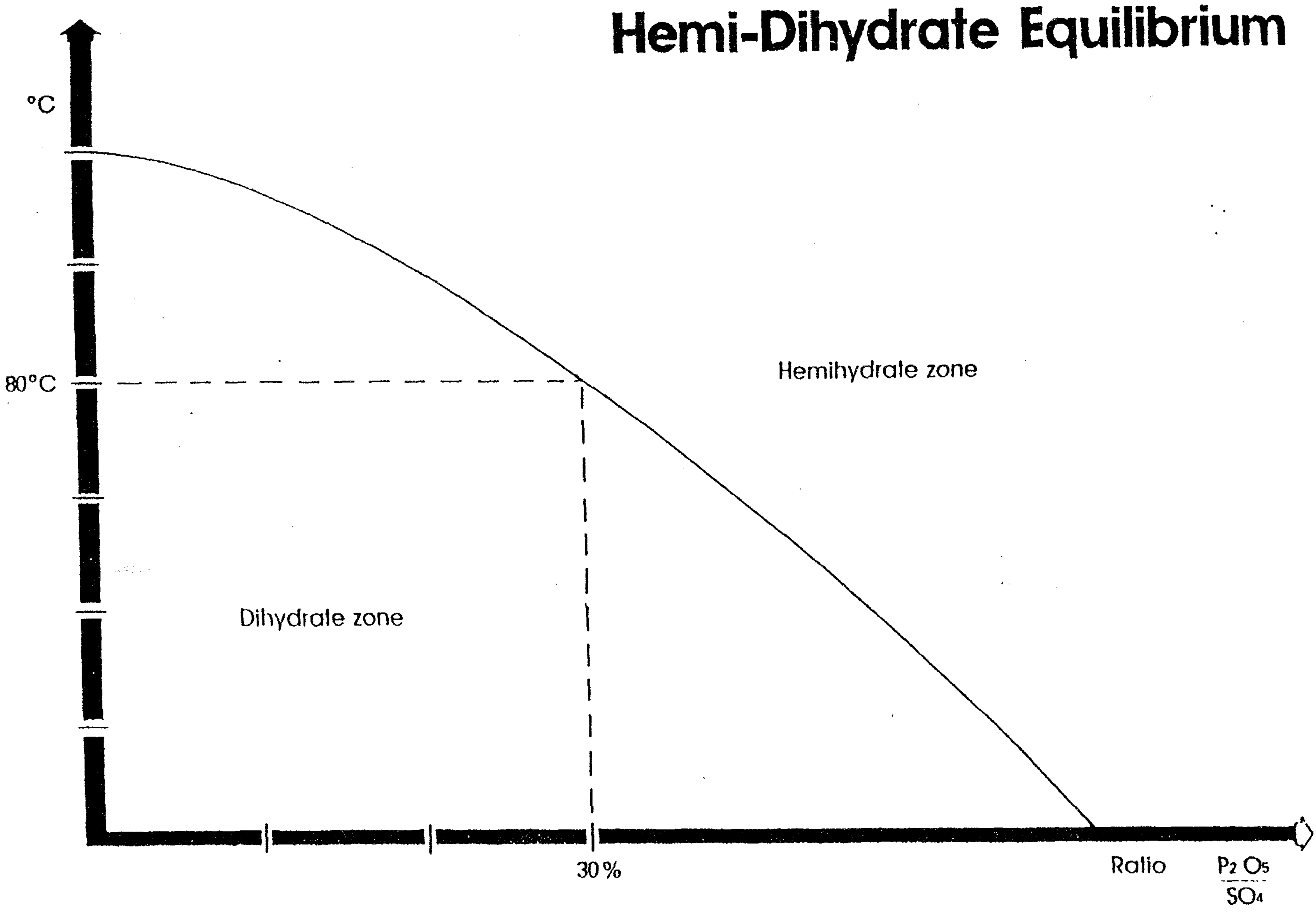

Hemi-Dihydrate Equilibrium
°C
80°C
Hemihydrate zone
Dihydrate zone
30 %
Ratio
$\frac{P_2O_5}{SO_4}$

fig IX

SURFACE ACTIVE AS PHOSPHOGYPSUM CRYSTAL HABIT MODIFIER IN PHOSPHORIC ACID WET PROCESS

by

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ABSTRACT

Brazilian phosphoric acid plants were designed to process sedimentary phosphatic concentrates, which have been replaced with native igneous concentrates since 1978. The igneous concentrate quality has gradually changed since that time, thus causing operational problems to the acid plants.

The main problem was related to the solubilization kinetics and phosphogypsum crystallization, which decreased the capacity by 20-25%. Even the P_2O_5 content in the reactor liquid phase was reduced from 29-30% to 24-26%, causing increased energy consumption in the concentration section of the plants.

Pilot plant research furthered by CENPES (PETROBRAS Research and Development Center) has demonstrated the benefits of additives on phosphogypsum filtrability, due to crystal shape and size modification. The best result was achieved with the addition of 200 ppm of surface-active agent to the phosphatic concentrate.

Industrial plant experiments have confirmed pilot plant research results, by increasing phosphoric acid production by 35%. The P_2O_5 content in the reactor has increased from 25% to 30%, thus reducing energy consumption in the concentration section by 45%.

INTRODUCTION

PETROBRAS - Petroleo Brasileiro S.A. holds the monopoly of petroleum exploration, production and research in Brazil. In addition, there are a number of subsidiary companies of PETROBRAS; to meet the country's needs in other fields. PETROBRAS subsidiary for the fertilizer field is PETROFERTIL - Petrobras Fertilizantes S.A.

PETROFERTIL has several companies, that are its majority shareholders, being responsible for the production of most basic inputs for fertilizer manufacture in Brazil.

In respect of domestic phosphoric acid production, three plants pertaining to the PETROFERTIL System have a yearly 500,000 tons. P_2O_5 output. Outside the PETROFERTIL System , two private enterprise plants produce another 200,000 tons. P_2O_5 per year.

These plants were originally designed to process imported sedimentary origin phosphate rock, such as Florida rock. Gradually, industrial production of phosphate rock from deposits located in Brazil was started, thus causing replacement of imported rock with native one.

In principle, such replacement has been successful, despite the fact that Brazilian phosphate rock is primarily igneous in origin. Some alterations to the operating parameters of the above-mentioned plants have been made, which allowed processing such igneous rock, maintaining the previous yield and production levels.

However, as changes at the mining faces occurred, processing difficulties in the phosphoric acid plants, such as drops in yield and production, have also arisen.

To overcome such difficulties, a number of studies on the chemical and mineralogical characteristics of the rocks are being conducted, also relating to the use of additives in the phosphate rock solubilizing stage.

One such study, jointly conducted by PETROBRAS, PETROFERTIL and GOIASFERTIL (one of PETROFERTILs affiliated companies, with an annual 1,000,000 ton phosphate rock production), addressed the use of a surface active compound as an additive in the rock solubilizing state, in order to modify the crystal habit of the gypsum formed in the process.

RESULTS OF TESTING CARRIED OUT WITH A SURFACE ACTIVE COMPOUND

This work was developed in two practical stages, respectively relating to pilot plant scale exploratory tests and later, to application of the results thus achieved to an industrial plant.

PILOT PLANT TESTING

This stage was preceded by an extensive bibliographic research, in order to update knowledge of the use of additives as crystal habit modifiers of the gypsum formed in phosphoric acid production plants.

After evaluating the existing publications on that subject, as well as the industrial experiences attempted in the country, it was concluded that one of the most promising additive type related to the group of surface active compounds.

From the information on the subject existing in the literature, a pilot plant scale testing program was developed, which, based on the differences encountered between the sedimentary origin ore considered in the literature and the Brazilian (igneous) rock, comprised a range of surface active compound concentration values, which were low as compared to those available in literature.

The test as performed have proved that the Brazilian igneous rock showed the same tendency as the heretofore used sedimentary rock. As can be seen from Figure 1, the rate of filtration achieved with the use of surface active compound gradually rises with increasing surface active compound content, until it reaches a maximum value. From this point on, a marked drop in the rate of filtration occurs, as the surface active agent content is further increased. Such drop is so fast and intensive, that the rate of filtration values fall below those achieved without the use of the surface active compound, as soon as the maximum point is surpassed.

In Figure 1, an increment of about 30% in the rate of filtration corresponding to the maximum point is noted, as compared to the value obtained without using surface active compound.

This experiment was conducted using an igneous phosphate rock sample from the GOIASFERTIL deposit at Catalao, in Goias State, which was designated Rock A, as in Tables I and II.

Figure 2 represents the repetition of the previous experiment, except that a different sample from the same deposit was used, as set forth in Tables I and II, and which was designated Rock B. It should be appreciated that the tendency shown in Figure 1 was fully corroborated in the second experiment. A shift of the point corresponding to the maximum rate of filtration value was observed, which then occurred at a different surface active agent content. Such fact is probably due to variation in the contaminants and their mineralogical forms, as different faces of the same deposit are being exploited.

By observing the gypsum crystals formed with the surface active agent addition, (Figure 3-B, C and D) a radical change in the crystal habit was found to have occurred. Crystals have become more homogeneous, with greater thickness and a smooth and even surface as compared to those obtained without surface active agent addition, which were lesser in thickness and had a rougher surface.

Crystals obtained without the use of a surface active agent have an elongated needle shape (Figure 3-A), with the length being three times the width dimension.

As the surface active compound content increased, a change in crystal shape could be observed. They showed a tendency towards reduction in length/width ratio, from 3:1 without surface active compound addition, to 2:1, as from the maximum points of Curves 1 and 2. After this point, increase in surface active compound content caused the formation of much smaller crystals, with a 1:1 length/width ratio and a nearly rounded shape, which characterized a near pulverization of the crystals.

Another change that took place was the increase in the rate of filtration with increasing surface active agent content, until a maximum value corresponding to the optimum surface active compound addition point was reached. After that point filtration rate values drop sharply, as the added compound concentration is raised. Such tendency can be clearly seen in Figure 1 and 2.

Further, the surface area values of the gypsum crystals formed were observed. At first, a drop in these values, from 3000 cm^2/g to about 2000 cm^2/g with surface active compound addition, took place. After the optimum point, as shown in Figure 1 and 2, the surface area values increased again, until the initial levels hab been reached.

TABLE I
CHEMICAL COMPOSITION OF ROCK BATCHES USED IN PILOT PLANT TESTING WITH ADDITIVE
% BY WEIGHT

COMPONENTS	ROCK A	ROCK B
P_2O_5	36.67	35.43
CaO	48.39	45.59
Fe_2O_3	2.31	2.26
Al_2O_3	0.73	0.50
MgO	0.49	0.98
BaO	0.83	0.67
SrO	0.92	0.95
SiO_2	1.93	3.00
TiO_2	0.77	1.39
MnO_2	0.14	0.10
Na_2O	0.25	0.29
K_2O	0.10	0.07
F	2.18	2.18

TABLE II
PARTICLE SIZE DISTRIBUTION ANALYSIS OF THE ROCK BATCHES USED IN THE PILOT-PLANT SCALE TESTS
% ACCUMULATED RETAINED MATERIAL

MESH	ROCK A	ROCK B
+ 65	10.28	7.94
+ 100	28.65	27.71
+ 150	44.18	44.67
+ 200	60.73	63.33
+ 270	73.34	77.71
+ 325	79.98	85.02
- 325	100.00	100.00

FIGURE 1

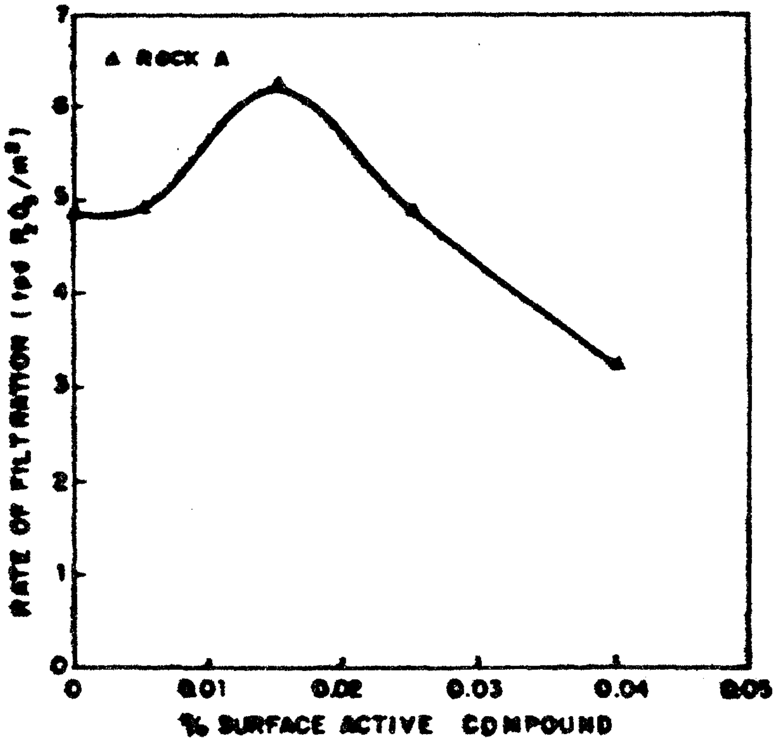


FIG. 1 - RATE OF FILTRATION VARIATION WITH SURFACE ACTIVE COMPOUND CONTENT

FIGURE 2

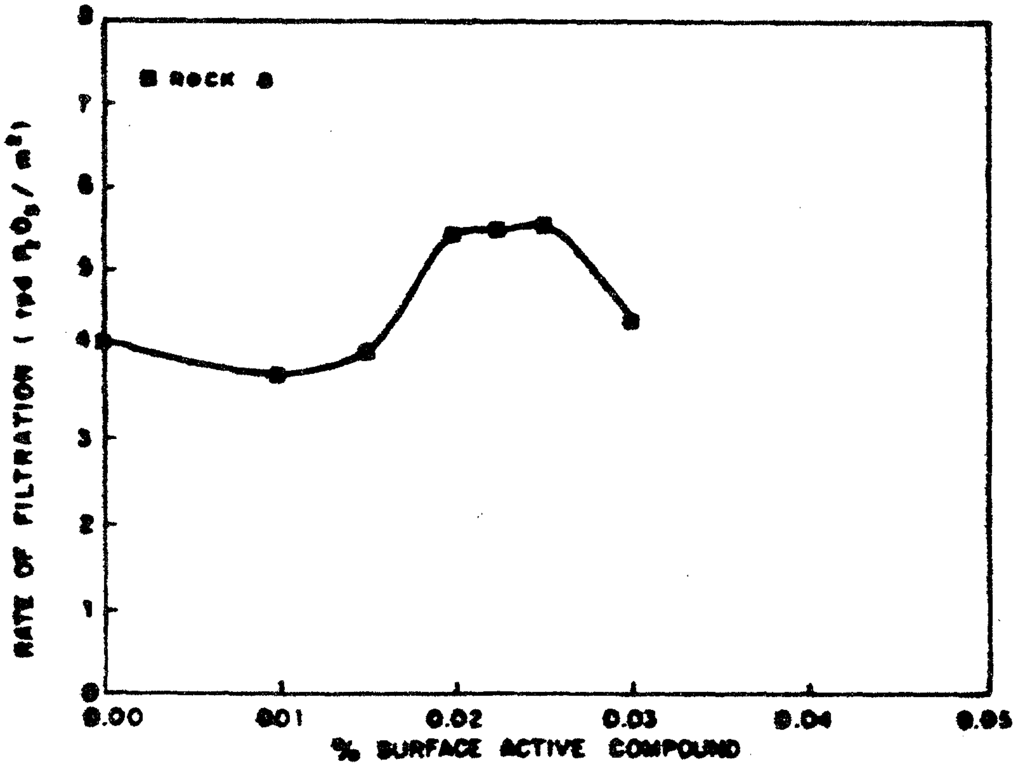
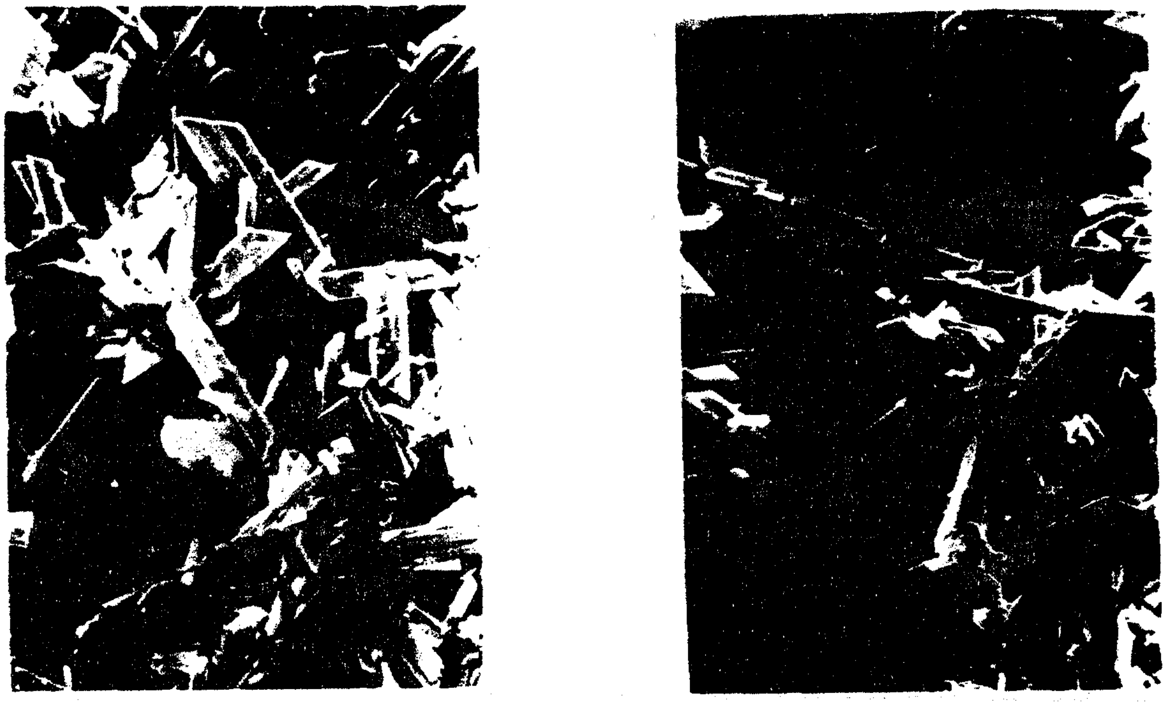


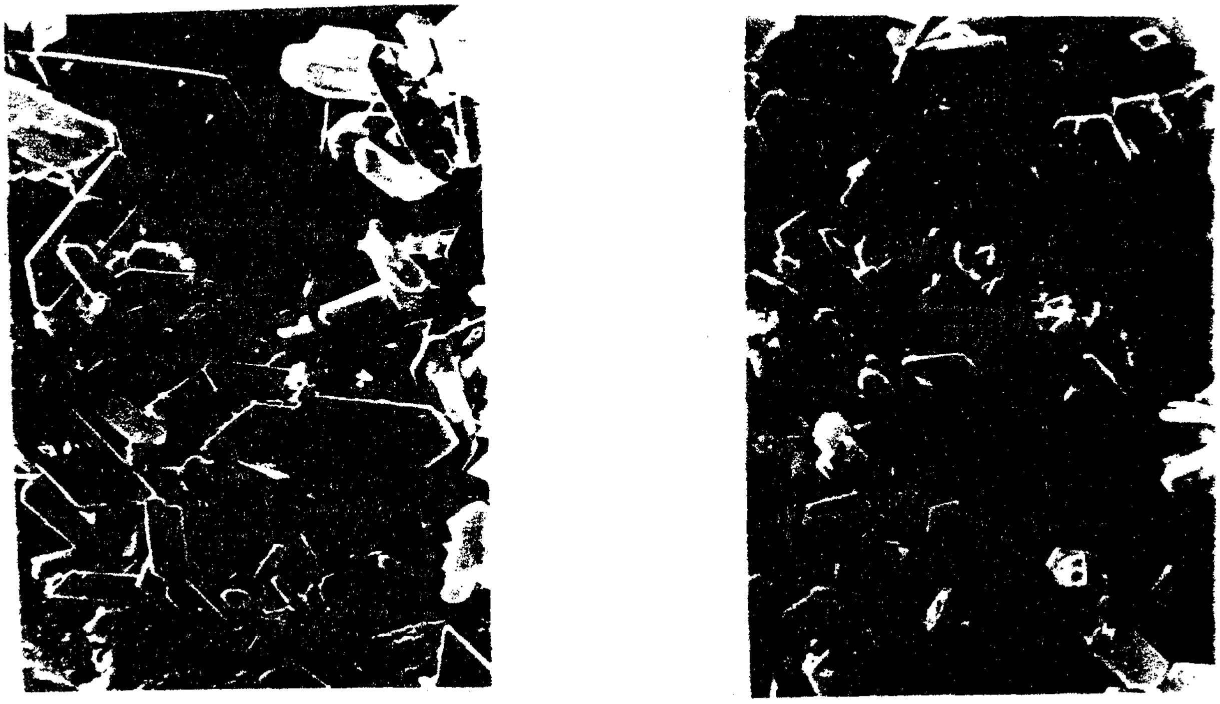
FIG. 2 - RATE OF FILTRATION VARIATION WITH SURFACE ACTIVE COMPOUND CONTENT

FIGURE 3
GYPSUM CRYSTALS FORMED IN PHOSPHORIC ACID PROCESS IN PILOT PLANT



A) WITHOUT SURFACE ACTIVE AGENT

B) WITH 150 PPM OF SURFACE ACTIVE AGENT (0.015%)



C) WITH 250 PPM OF SURFACE ACTIVE AGENT (0.025%)

D) WITH 300 PPM OF SURFACE ACTIVE AGENT (0.030%)

TEST CONDUCTED AT AN INDUSTRIAL PLANT

From the results obtained in pilot plant scale testing, a test at the ULTRAFERTIL industrial phosphoric acid production plant, located at Cubatao, Sao Paulo State, was scheduled.

This plant was designed for an output of 75,000 tons per year of P_2O_5, using DORR-OLIVER technology and phosphate rock imported from Florida.

The plant, after the Florida rock had been replaced with the GOIASFERTIL rock, operated for two years, maintaining design production and recovery levels.

With the changes occuring at the GOIASFERTIL deposit mining fronts, contaminant levels and mineralogical forms were significantly altered, causing a sharp drop in production and/or recovery levels of the phosphoric acid plant.

The industrial test as performed has inequivocally proved all of the tendencies observed during the pilot plant scale testing. The test was continued for 45 days, and as in pilot testing, the surface active agent content within the reactor was gradually raised, until reaching a maximum operating efficiency point.

The ideal surface active compound addition level at the industrial plant was equivalent to the value found at the pilot plant. These ideal operating conditions represented a 35% increment in production, about 20% increase in concentration of the acid exiting the filter and energy savings in the order of 42% in the acid concentration section.

Tables III and IV show the chemical and mineralogical analyses of the phosphate rock employed in the ULTRAFERTIL industrial tests. Those analyses did not evidence any significant differences relative to the rock that was normally used in the ULTRAFERTIL phosphoric acid plant.

Table V shows the characteristics of the surface active compound used in pilot plant and industrial plant tests.

Table VI sets forth the average operating conditions of the ULTRAFERTIL plant during industrial test performance.

Process losses in the reaction and filtration stages, as regards P_2O_5 , were kept practically constant, irrespective of surface active compound addition. Industrial efficiency remained around 95.

TABLE III
CHEMICAL COMPOSITION OF THE ROCK BATCHES USED IN THE INDUSTRIAL TEST
% BY WEIGHT

COMPONENTS	ROCK C (WITHOUT ADDITIVE)	ROCK D (WITH ADDITIVE)
P_2O_5	36.28	36.23
CaO	48.73	45.65
Fe_2O_3	2.48	2.48
Al_2O_3	0.37	0.30
MgO	0.52	0.53
BaO	0.30	0.53
SrO	0.88	0.86
SiO_2	2.76	2.78
TiO_2	0.83	0.83
MnO_2	0.09	0.08
F	2.49	2.49
INSOLUBLE RESIDUE	4.56	4.91

TABLE IV
PARTICLE SIZE DISTRIBUTION ANALYSIS OF ROCK BATCHES USED IN THE INDUSTRIAL TEST
% ACCUMULATED RETAINED MATERIAL

+ 65	4.3	4.3
+ 100	18.5	18.9
+ 150	40.2	41.0
+ 200	58.3	60.7
+ 325	77.7	78.8
- 325	100.00	100.00

TABLE V
CHARACTERISTICS OF THE ADDITIVE (SURFACE ACTIVE COMPOUND) USED IN THE PILOT-PLANT AND INDUSTRIAL TESTS

COMPOUND:	DODECYL BENZENE-SULPHONIC ACID
APPEARANCE:	REDDISH-BROWN VISCOUS OIL
PURITY DEGREE:	MIN. 94%
FREE H_2SO_4 CONTENT:	MAX. 2.0%
ACID NUMBER:	180 to 230 mg KOH/g
H_2O (WATER):	MAX. 1.5%
FREE OIL:	MAX. 3.0%
Ca AND Mn:	MAX. 2.0%
MANUFACTURER:	HENKEL S.A.

TABLE VI
OPERATING PARAMETERS DURING THE INDUSTRIAL TEST DIHIDRATE PROCESS - DORR-OLIVER TECHNOLOGY

PARAMETERS	WITHOUT ADDITIVE	WITH ADDITIVE
SPECIFIC VOLUME (m^3/tpd P_2O_5)	2.5	1.6
REACTION TEMPERATURE (^oC)	79	81
REACTOR P_2O_5 ACID CONTENT (%)	24.5	30.0
REACTOR SOLIDS CONTENT (%)	25	30
SULPHATE CONTENT (%)	3.0 - 3.2	3.0 - 3.2
GYPSUM SSA (cm^2/g)	3400/4000	2000/2500
TOTAL P_2O_5 LOSSES IN GYPSUM (%)	0.89	0.88
REACTION EFFICIENCY (%)	97.04	97.03
FILTRATION EFFICIENCY (%)	99.26	99.28
PROCESS EFFICIENCY (%)	96.32	96.33
VAPOR (tons/tón P_2O_5)	2.1	1.0
ENERGY FACTOR (Gcal/ton P_2O_5)	1.8	1.0
ADDITIVE DOSING (g/ton rock)	-	250/300

CONCLUSIONS

The main conclusion arrived at after performance of the pilot-plant scale and industrial plant tests, was that the additive, surface active compound dodecyl benzene sulphonic acid markedly changes the crystal habit of the phosphogypsum formed during Brazilian igneous phosphate rock processing, obtained from GOIASFERTIL, for the production of phosphoric acid.

This crystal habit modification of the phosphogypsum occured in a positive manner and provided and increase in the P_2O_5 production capacity of the industrial plant as well as significant energy saving in the phosphoric acid concentration stage.

The ULTRAFERTIL industrial plant continues to use the surface active additive with efficiency, and operating at 110% nominal capacity.

ACKNOWLEDGMENTS

We are grateful for the participation of PETROFERTIL, GOIASFERTIL, and ULTRAFERTIL in the joint pilot-plant and industrial plant scale testing program development, as directed to the improvement of GOIASFERTIL Brazilian phosphate rock processing.

REFERENCES

Leyshon, D.H. et al., 1965 - Manufacture of Phosphoric Acid United State Patent No. 3 192 014.

SULFUR DIOXIDE FROM PHOSPHOGYPSUM BY A FLASH PROCESS

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ABSTRACT

A process is being developed for recovery of sulfur dioxide from phosphogypsum, for recycle into the wet phosacid process. Dried gypsum mixed with smaller amounts of pulverized coal, pyrite and other minerals is sprayed by compressed air into a flame. Excess fuel reduces the sulfate, releasing SO_2 to the product gas. The minerals fuse together and drain from the reactor as a molten slag. The slag is quickly quenched to form hard, nonporous lumps of glass that resist leaching and radon release.

This "FLASC" process consumes cheap high-sulfur agglomerating coals without prior conversion to coke. It seeks to minimize unit capital costs with very fast conversion. Dried phosphogypsum is used directly, without particle size alteration. The volume of solid to be disposed of is reduced to about half, while overcoming environmental liabilities of untreated phosphogypsum.

This approach has been tested successfully at laboratory scale, with up to 19% SO_2 in dry product gas. It is being tested further in a small pilot plant.

INTRODUCTION

PROJECT GOALS

About 500 million tons of phosphogypsum have been dumped in gypstacks in the US. Sulfur costing nearly $1 billion/year is locked in this waste, which grows by about 40 million tons/yr. There would be great economic and environmental benefits if the sulfur values could be recovered for recycle to the phosacid plants, and if the solid waste could be reduced or eliminated.

Means to do this has been sought for many years and in many countries. Most of the effort has been directed at high temperature reduction with excess fuel to produce either sulfur dioxide, or solid sulfur with CaS as an intermediate. Various process configurations have proven technically successful, but economically unattractive. Conventional sulfur burning has almost always been cheaper than recycle from gypsum, primarily because of high fuel and capital costs.

We have investigated a new process configuration for thermal reduction of phosphogypsum to produce SO_2. Unlike most previous efforts, we have not adapted conventional equipment for phosphogypsum feed. A process configuration tailored specifically for this task was developed based on a combination of computer modeling and laboratory tests.

The goal is to minimize fuel costs by designing for very low-cost fuel, and to minimize the capital cost component with *very* fast conversion. The solid byproduct is a nonporous vitreous slag, that overcomes most environmental concerns with untreated phosphogypsum.

PROCESS CONFIGURATION

Our process configuration is named FLASC, for Flash Sulfur Cycle. Predried gypsum and pulverized coal are sprayed with compressed air into a flame. Char is gasified, and most of the SO_2 release takes place while individual particles are suspended in gas. Particles are then caught in a layer of molten slag, where they fuse together and complete their SO,-releasing reactions. The slag drains into water, where it is quickly quenched to form lumps of glass.

Gas exits the reactor roughly 2 seconds after introduction. Retention time for slag is longer, but, the slag occupies little volume. Consequently, conversion is rapid compared to a fixed bed of similar size for example. It is hoped that fast conversion will translate into low unit capital costs.

Product gas laden with SO_2 is cooled as heat is recovered. After drying and HF removal, the gas recycles to conventional sulfuric acid production. One of our goals is SO_2 concentration sufficient for use in existing sulfur-burning sulfuric acid plants.

FEED MATERIALS

Pyrite is included in the feed mixture to boost SO_2 concentration and reduce the slag fluid temperature, as well as for fuel value. Low cost, high sulfur bituminous or subbituminous coal is the fuel of choice. Some SiO_2-bearing mineral such as clay may be added as flux, depending on quality of the other feeds. It is possible that impure coal or coal cleaning wastes can contribute some of the pyrite, SiO_2 and fuel.

Phosphogypsum typically contains most of the necessary SiO_2 as impurities. The phosphogypsum is used without particle size alteration (grinding or pelletizing) except possibly for separation of the largest particles.

PROJECT STATUS

An 18-month laboratory test program sponsored by FIPR ended March 1989. Computer simulations of product equilibria, and material and energy balances were developed as design aids. The slag fusion phase diagram was investigated with crucible tests in a controlled atmosphere. Refractories were tested for durability in contact with simulated product gases and molten slag. Then a 2-liter reactor was built for physical simulation of expected entrained slagging conditions.

Experimentation with the laboratory reactor demonstrated consistently over 98% desulfurization and carbon utilization with 1 to 2.5 sec gas retention times. Slag formed and drained without difficulty. The slag was hard, glassy, chemically unreactive, and resistant to leaching. It trapped nearly all of the radon that untreated phosphogypsum would release.

Based on these encouraging results, a small pilot plant was built with FIPR support, and later US EPA co-funding. It was completed and first tested in May, 1990. Its 60 liter (2.1 cu ft) reactor is designed for up to 40 lb/hr conversion.

The pilot plant design is based on results of the laboratory testing. Its purpose is testing of the FLASC process concept in conditions that more realistically represent expected commercial conditions, development of engineering design data for scale up, production of slag for testing, and evaluation of economic merits.

If FLASC continues to show promise, we hope to develop it further in cooperation with a phosphate company(s), or with one of their supporting engineering firms.

FLASC PROCESS DESIGN FUNDAMENTALS

Processing conditions were selected after study of reaction enthalpies and chemical equilibria among the reactants and products. Further design guidance was provided by a computer simulation based in part on these thermodynamic data. Test results from our 2-liter reactor also yielded essential design information. They confirmed that reactions are fast, that slag-resistant refractories exist, and that slag forms and drains readily. The pilot plant design was based on the foregoing information developed in the course of this project, in conjunction with personal experience and published literature on related slagging coal gasifiers and flash copper smelters.

The following sections discuss the reactions, the slag phase diagram, thermodynamics and equilibria, and the computer model. Model results are used in preliminary economic projections.

PROCESS CHEMISTRY

Reactions and Products

Gas-particle reactions can be written, roughly in the sequence they occur on fresh feed particles:

$\text{coal} \rightarrow C + \text{volatiles}$ **Devolatilization** 1)
$FeS_2 + 2\tfrac{1}{2}O_2 \rightarrow FeO + 2SO_2$ **Combustion** 2)
$C + O_2 \rightarrow CO_2$ 3)
$C + CO_2 \rightarrow 2CO$ **Char Gasification** 4)
$CaSO_4 + CO \rightarrow CaO + SO_2 + CO_2$ **Gypsum Reduction** 5)

The water gas shift reaction is very fast in these conditions and is always near equilibrium. Hydrogen is essentially interchangeable with CO in reactions 4 and 5.

$H_2 + CO_2 \leftrightarrow H_2O + CO$ **Water Gas Shift** 6)

Before the suspended particles are carried out with product gas they are caught in the slag layer, where they complete their chemistry.

$2CaO + SiO_2 \rightarrow Ca_2SiO_4$ **Silicate Formation** 7)
$2FeO + SiO_2 \rightarrow Fe_2SiO_4$ 8)
$2Ca_2SiO_4 \leftrightarrow CaSiO_3 + Ca_3SiO_5$ **(etc.)** 9)

Gas also continues to react with incompletely-converted materials in the slag according to reactions 4 and 5 above. The product silicates are a vitreous mixture which is approximately represented by the olivine products of reactions 7 and 8. The silicate mixture includes molecules with both greater and lesser SiO_2 proportions as is indicated in reaction 9, and it varies with the proportion of SiO_2 in feeds.

Sulfide formation is possible in abnormal conditions of low temperature or great fuel excess. The sulfide of iron (troilite, FeS) is thermodynamically favored over calcium sulfide. Troilite is found in natural rocks, while CaS is not.

$SO_2 + FeO + 3CO \leftrightarrow FeS + 3CO_2$ Sulfide 10)

H_2S and COS are not included in the reaction equations because they were not produced experimentally. A final reaction is written to account for magnetite, which is expected on thermodynamic grounds and was found experimentally in minor amounts. Magnetite is also produced in related copper smelter slags. This is a high-melting crystalline phase with low solubility in the silicate mixture.

$1\tfrac{1}{2}Fe_2SiO_4 + 1\tfrac{1}{2}Ca_2SiO_4 + 4CO_2 \leftrightarrow Fe_3O_4 + 3CaSiO_4 + 4CO$ 11)

These reactions form a theoretical framework with which to interpret experimental results, estimate heat requirements and equilibria, and to make projections. The detailed reaction mechanisms and pathways are unknown and are no doubt more complex.

Thermodynamics

Heats and equilibrium constants of selected reactions are listed in Table 1. Note that gypsum reduction reaction 5 is strongly endothermic. Consequently, fuel requirements are high for FLASC as well as all related processes.

TABLE 1. Reaction Thermodynamics
Computed at 1427°C

REACTION	ENTHALPY (Kcal/mole)	$\log_{10}$ of EQUILIBRIUM CONSTANT
2	-167.1	20.72
3	-94.65	12.18
4	38.91	3.84
5	46.58	1.60
6	6.79	.52
7	4.39	3.27
8	-1.06	2.38
11	-52.19	-1.94

SLAG FUSION BEHAVIOR

A slagging approach to SO_2 recycle requires that the condensed products fuse to form a fluid that can drain freely by gravity at a temperature that practical lining materials can withstand., Calcium oxide by itself is very high-melting, so additional fluxing minerals are required to promote slag formation. Iron pyrite not only serves as flux, but also adds makeup sulfur and fuel value, and improves product gas SO_2 concentration. Silica sand or other SiO_2-containing minerals may be added as fluxes. For example, dried clays, scrap glass, scrap brick, diatomaceous earth, coal ash, or coal cleaning waste may be added to adjust slag SiO_2 content.

Fusion behavior of product slag is predicted approximately by the ternary phase diagram of its principal oxides in Figure 1. Of course, slag is not truly ternary, because it contains lesser amounts of other oxides. Our lab tests found softening and fusion over a range of temperatures that were always less than Figure 1 suggests. Also, the fluxing effect of FeO was greater than is indicated in the figure. Nevertheless, Figure 1 is useful to illustrate relative changes in fusion temperature in relation to slag composition.

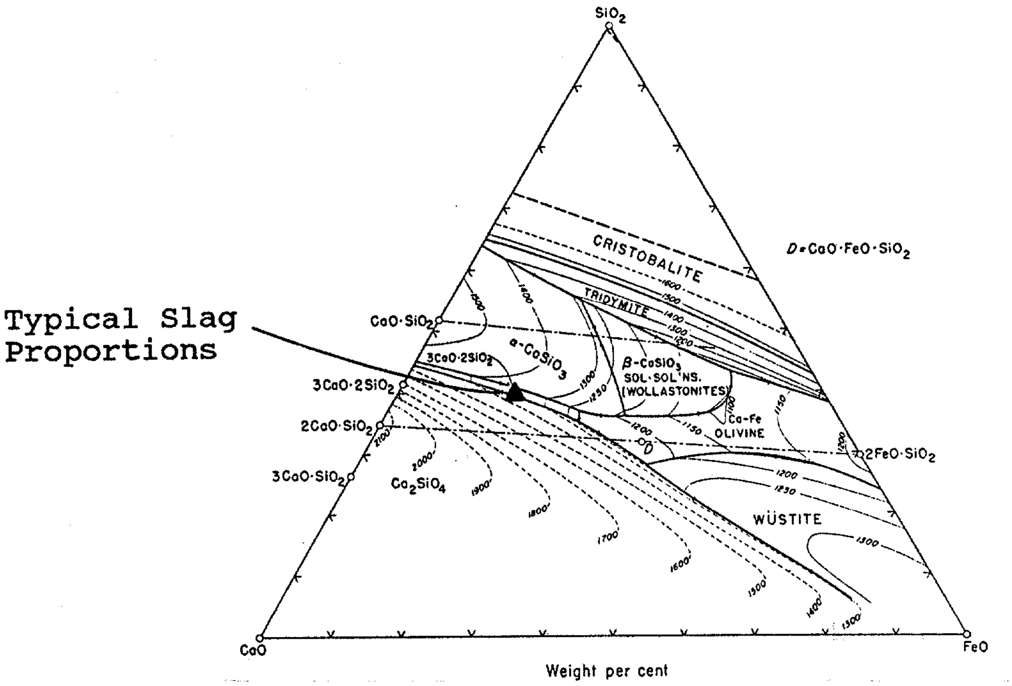

FIGURE 1. Ternary phase diagram for the system CaO-FeO-SiO$_2$. From J. Am. Ceramic Soc. 38, 264, 1955.

At 45% SiO$_2$ and 55% CaO there begins a valley of low-melting eutectic mixtures extending toward the FeO corner. To maximize gypsum conversion while keeping the slag fluid, slag oxide proportions should fall in or slightly below this valley. Optimum FeO content will depend largely on pyrite costs, but some FeO appears to be essential to fusion. A typical slag composition that would be reasonable for commercial processing is marked on Figure 1 as a triangle.

REACTION EQUILIBRIA

A multiphase chemical equilibrium model was used to predict the reaction product mix and its dependence on feed proportions, temperature, and pressure. The equilibria were computed by FORTRAN program BOBKAT, descended from the Stanford Research Institute TIGER code. Product concentrations are computed at specified temperature and pressure so that the total Gibbs free energy of the assemblage is minimized.

Product Gases and Slag Species

Preliminary calculations were done to identify the range of potential product species. Carbonyl sulfide, OH and certain other gas species have been eliminated as potential products because preliminary calculations or tests showed minor concentrations and negligible influence on major species equilibria.

Condensed species that were never predicted as products in a reasonable range of slagging conditions were omitted from subsequent calculations. Thus, carbon, SiO_2, Fe, FeO, Fe_2O_3, CaS, and $CaSO_3$ were eliminated. Ca_3SiO_5 appears only in calcium-rich equilibria. Unreacted $CaSO_4$ is predicted only for very low temperature and/or fuel-lean conditions. Magnetite Fe_3O_4 that is found in related copper smelter slags, is also predicted by BOBKAT simulation. It was found experimentally by X-ray diffraction as part of the 5% crystalline content of a FLASC slag.

These equilibrium product predictions are approximate because heats of fusion and other thermodynamic data are not precisely known for all species at high temperature. Also, condensed species are treated as individual ideal crystalline phases or immiscible liquids, neglecting nonideal mixing and solution effects. Solution effects tend to stabilize condensed species that would otherwise disappear at unit crystalline activity, so that they change concentration with temperature more gradually and smoothly than BOBKAT equilibria predict.

Equilibrium modeling assumes complete mixing and ample time for reaction. The latter approximations were supported by test results, except that quartz grains dissolved incompletely in some of our slags produced below about 1320°C.

Sample Equilibria

With these caveats, the equilibrium calculations are very useful in predicting major and minor species among the products, which reactions approach completion, and which reactions are significantly reversible. Table 2 shows the predicted product species and amounts for a representative feed mixture at 1427°C (1700°K) and 1 atm pressure. Oxide proportions for these calculations correspond to the triangle in Figure 1.

Effects of Variation in Temperature and Air Proportion

How does process performance vary with reaction temperature and fuel/air ratio? A series of equilibria were computed to examine these responses.

Holding other conditions constant, the amount of air was varied in steps. For each step, equilibria were computed from 875° to 1700°C. Figure 2 shows computed SO_2 concentrations in mole percent for different proportions of reductant. "Oxygen Demand" values in Figure 2 were computed by comparing total oxygen, X, in the mixture with the amount needed to form normal oxides from all other elements, Y. For this calculation, carbon, sulfur and iron oxides were taken to be CO_2, SO_2, and FeO. Oxygen demand equals 1 - X/Y.

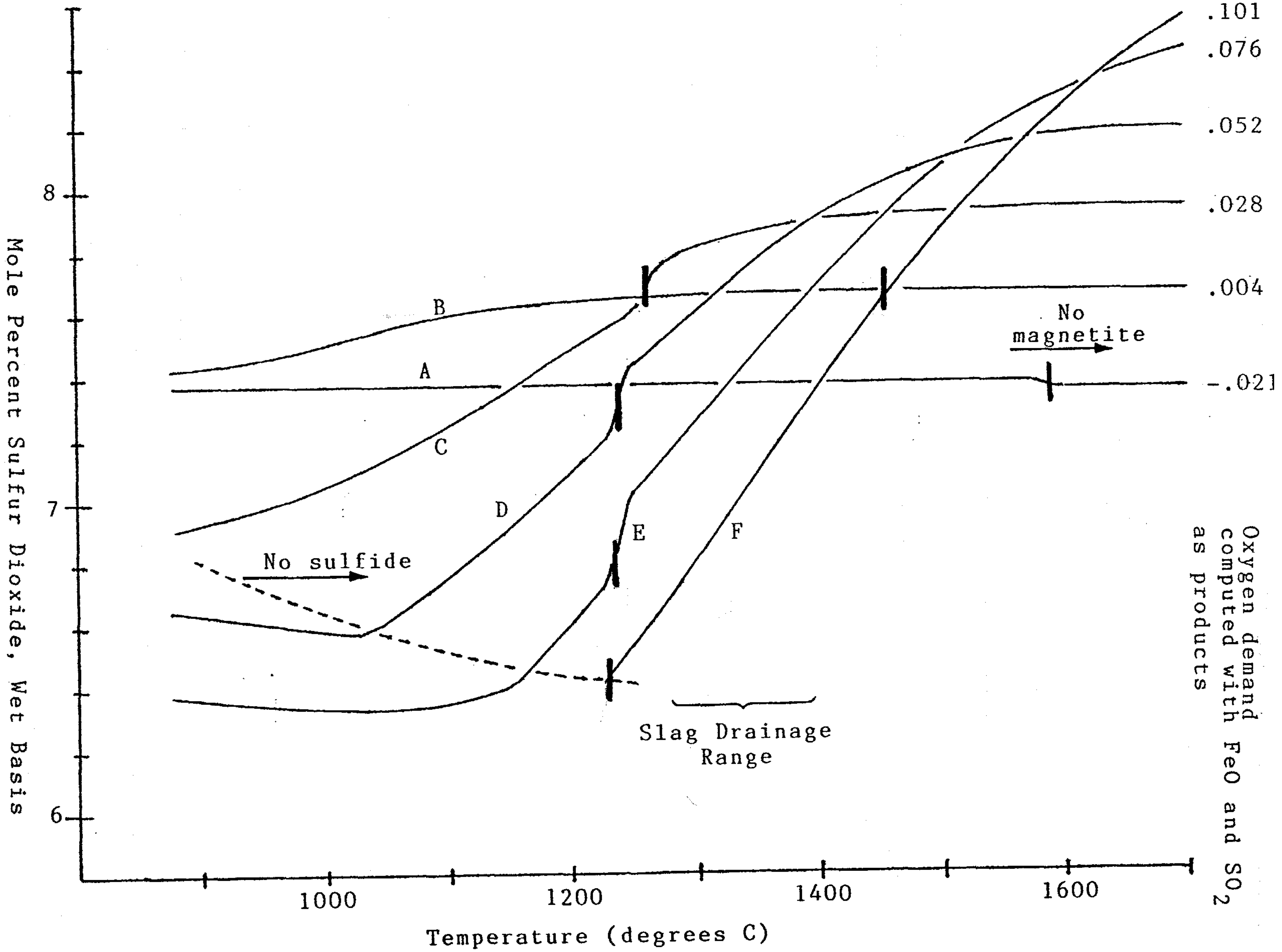

FIGURE 2. Equilibrium Sulfur Dioxide Concentration in Product Gas as a Function of Temperature and Mixture Proportion

Table 2. Predicted Equilibrium Product Species at 1400°C

Gas Species	Percent by Volume
Nitrogen	67.8
Sulfur Dioxide	7.90
Carbon Dioxide	15.4
Water Vapor	6.88
Carbon Monoxide	1.73
Hydrogen	.24
Sulfur vapor, S_2	.017
Hydrogen sulfide	.0055

Liquid Species	Wt. Percent
$CaSiO_3$	47.8
Ca_2SiO_4	26.2
Fe_2SiO_4	19.2
Other Oxides	6.8

Mass Ratio Slag/Gas = 187/813 = .230

Values in Table 2 were taken at 1400° on curve C. This proportion of air/fuel is near optimum because it produces high SO_2 concentration without sulfide or magnetite in the temperature range typical of slag drainage (1275-1400°C).

Vertical slashes through each curve illustrate temperature maxima for magnetite in the slag. The dashed line in Figure 2 indicates maximum temperatures for sulfide. Sulfide formation represents a potential loss mechanism for sulfur and fuel values. However, no sulfide is predicted above about 1250°C, even for the most strongly reducing mixture. At mildly reducing conditions like those of curve C, no sulfide is predicted even at 875°C. This was supported by lab test results, where slag sulfide was too small to measure in all but one sample. The exception contained 0.31% S and was produced in strongly reducing conditions, with 0.11 oxygen demand at 1320°.

Although BOBKAT predicted a fraction of a percent each of H_2S and S_2 in the gas, they have not been found experimentally under normal conditions. Kinetics of their formation may be slow, or they may be consumed by secondary reactions in cooling product gas.

PROCESS SIMULATION

We have developed a computer model to simulate FLASC process performance at both commercial and lab scale. This lumped-parameter simulation neglects reaction rates and spatial distribution in the reaction chamber. The reactor is treated as a well-mixed black box at steady state. Product mixtures are computed from element and energy balances, together with equilibria of the water gas shift and sulfide-forming reactions and the proportion of air. This PC-compatible FORTRAN program is named LYNX.

Model Assumptions

Slag products include either $CaSiO_3$ or Ca_3SiO_5 along with Ca_2SiO_4, depending on Ca/Si proportions. Calcium sulfate is neglected because it is stable only in abnormal conditions of low temperature and/or insufficient fuel. Magnetite is not included as a product. This omission has no effect on major oxide proportions, and negligible effect on the energy balance. FeS is included as a potential product.

Model Inputs

The reactor simulation accepts as input a specified point on the quasi-ternary phase diagram of Figure 1. Using detailed analyses of the phosphogypsum, pyrite, sand and coal ash, LYNX computes the proportions of these feeds that lead to the specified weight percents of FeO and SiO_2 in slag. "Sand" here designates any SiO_2-containing mineral flux.

Feed material compositions are expressed in terms of the eleven chemical compounds listed near the beginning of LYNX sample printout, in the Appendix. Contributions of minor components such as pyrite and silica in coal minerals are properly accounted for this way in the material and energy balances and the ternary melting phase diagram. Chemical species proportions are expressed in moles per 100 grams of feed mixture. "Ash" represents all minor metal oxides.

LYNX inputs also include feed and product stream temperatures in degrees C. They are used in conjunction with the energy balance to compute fuel requirements. It has been assumed in this simulation that heat is recovered from product gas to preheat the process air. Recovered heat also drys and preheats the gypsum, which is premixed with sand in this example.

LABORATORY TEST RESULTS

TUBE FURNACE TESTS

Crucible tests in a controlled atmosphere tube furnace were used to explore the slag melting phase diagram and identify promising proportions of feed materials. Direct observation of melting samples yielded understanding of softening and fluidity, viscosity f and foaming behavior. The 1320°C tube furnace was also used to test refractory materials for resistance to the corrosive effects of our slag and product gas.

SLAGGING ENTRAINED REACTION CONDITIONS

A 2-liter entrained-flow slagging reactor was built to test high-speed processing conditions. The reaction chamber is 11.4 cm diameter and 18 cm high. The surrounding cavity can be heated electrically to over 1650°C. Premixed feed solid was sprayed from a top central nozzle surrounded by four small propane-air burners. Slag and gas exited through a bottom central tap hole. Air was supplemented in some tests with bottled oxygen.

Reductant proportions were controlled via propane and oxygen or air flows, and reaction temperature was monitored with an optical pyrometer. Grab samples of product gas were collected at intervals for later Orsat analysis for CO_2, SO_2 and CO. Slag and elutriated dust were sampled batchwise after each run period. They were analyzed by standard wet chemistry, beginning with solution in HF.

A series of entrained slagging tests were performed on this equipment at the laboratory scale in the fall of 1988 through early 1989. Three preliminary tests did not produce slag or gas samples in amounts sufficient for analysis, so these runs will not be discussed here. The remaining four runs each did produce significant slag and/or gas. Problems with nozzle overheating limited run time and interfered with systematic testing until the last run, when the nozzle problem was solved. Only the final run achieved a completely steady state. Nevertheless, the laboratory test program produced quite useful results.

ENTRAINED SLAGGING RESULTS

Slag draining freely from the entrained reactor tap hole usually contained moderate void, suggesting nearly complete reaction and gas release. Slag produced with proper conditions contained no detectable sulfide, and very little sulfate. Both X-ray diffraction and thin-section polarized microscopy showed that gypsum and pyrite in the reactants are completely consumed, and that the slag is about 95% noncrystalline. Slag hardness was always between 5.5 and 6.5 on Mohs' scale, which is comparable to iron or window glass. Desulfurization of the slag was never less than 98% complete, and carbon utilization was typically 99%.

The following sections report data for each of the four periods of reactor operation. The first period produced four gas samples, but no slag. Period 2 produced only slag. Periods 3 and 4 produced both gas and slag samples. The final run encompassed multiple steady states, and gas samples are reported for each of them individually.

Product Gas Composition

Table 3 reports data on gas samples. Oxygen demand was defined above in connection with the BOBKAT equilibrium model and Figure 2. To evaluate SO_2 recovery, a dimensionless parameter "theoretical SO_2" is defined as follows: total mmoles/sec of sulfur atoms entering the process with solid feeds is divided by total dry product gas mmoles/sec. This would equal the measured dry gas SO_2 concentration at steady state if all sulfur atoms were produced as SO_2. The fraction of theoretical SO, produced experimentally is a figure of merit.

Table 3. Run Conditions and Product Gas Composition

Run Period	1				3	4			
Run Time (minutes)	35				55	285			
Pyrometer Temperature (°C)	1255	1255	1270	1283	1355	1308	1288	1293	1320
Product Gas Sample	1a	1b	1c	1d	3	4a	4b	4c	4d
Retention Time (sec)	1.3	1.3	1.6	2.2	1.1	1.0	1.0	1.0	1.3
Oxygen Demand	.025	.025	.067	.108	.01	.00	-.10	.03	.11
Theoretical SO_2, %	10.1	10.1	9.2	12.9	4.4	1.8	1.8	1.8	2.4
SO_2 (volume %, dry)	5.4	5.8	9.9	19.0	4.4	1.0	.6	.5	2.3
CO_2 (volume %, dry)	18.1	17.5	20.4	14.2	10.0	7.9	7.3	5.7	13.6
CO (volume %, dry)	<.2			<.2	1.3	1.5	.7	.7	2.2

Nitrogen was used in place of nozzle air during runs 3 and 4 as part of a strategy to avoid nozzle overheating. Consequently the product SO_2 was considerably diluted to a much lower theoretical steady state maximum.

Gas SO_2 typically approached the theoretical steady state concentration when mixture proportions were significantly reducing, and fell below it in neutral or oxidizing conditions. In the transient conditions of period 1, a sample with 147% of theoretical steady state SO_2 was produced. This is due to solidified slag accumulated on the hearth that was desulfurized in a short period when oxygen demand was raised from .025 to .108, and pyrometer temperature went from 1255 to 1283°.

In spite of these substantially reducing proportions, less than 0.2% CO appeared in the product gas. Gas reducing values were almost completely consumed by reactions producing the 19% SO_2 in that sample. Gas reaction with the slag pool must have been rapid to explain this result.

The slag that had accumulated on the hearth in periods 1 melted and drained completely at about 1380^{0} in period 2. The hearth was undamaged, with no sign of erosion.

Conditions in the fourth run varied from substantially oxidizing in period 4b to substantially reducing in period 4d. During period 4d, SO_2 concentration approached its theoretical value and CO rose to 2.2%. It is likely that sulfur vapor, found condensed in the dust, was produced primarily in the period 4d conditions. The generally excellent slag desulfurization shows that reactions approach completion even for off-spec feed proportions. Reductant control seems to be less critical than is predicted by the BOBKAT model.

<u>Product Slag Composition</u>

Table 4 reports the result of analyses on the slag. Slag analysis of the fourth run should be interpreted in relation to conditions during the entire composite run, which totals more time than the four gas sampling periods shown above.

Table 4. Product Slag Analyses

Run Period	2	3	4
Mohs Hardness	6.0	6.0	6.0
Mean Density (g/cc)	1.7	3.3	2.0
Density Range (g/cc)	1.6-2.7	NA	.98-2.5
Total Sulfur (% SO_3)	.02	.11	.76
Sulfide (% S)	trace	0	0-.31
Carbon (%)	.50	.03	.04
Iron (% FeO)[a]	17.9	18.6	18.2
Calcium (% CaO)[b]	17.8	15.7	19.4
HF-insolubles, %	3.7	1.0	1.1

a The FeO value includes Al_2O_3, TiO_2 and PO_4.
b The CaO values are lower than expected and are suspect.

Slag produced in neutral or reducing conditions (oxygen demand >0) near steady state (runs 3 and 4) contained unconverted sulfate ranging from 0.11 to 0.76 % SO_3. The higher figure corresponds to minimum 98% removal of the sulfur in feed gypsum. Desulfurization of the slag was always > 98% even with 1 sec gas retention time.

The only quantitative slag sulfide measurement was done on period 4 slag. This was on the slag sample with the strongest H_2S odor on HF contact with pulverized sample. It probably corresponds to the strongly reducing period 4d conditions. Using calcium as a tracer for estimation purposes, this sulfide represents 1.4% of the sulfur in feeds.

Voids form and burst as the molten slag completes its gas releasing reactions. Voids always had the form of closed spherical bubbles. Longer slag retention times allow for more complete gas release and denser slag. In these tests, slag drained freely across the flat hearth to the tap hole. Its retention time was unknown and probably not more than a minute.

The slag from period 3 had little void space, approaching crystal grain density. At the other extreme, certain low-density samples produced during period 2 contained up to 70% void volume, showing evidence of continuing rapid gas release. The latter samples may have been produced from nearly-fresh feed material stuck to the tips of overheated nozzles, dropping directly through the tap hole. Overheated nozzles always bore evidence of melt dripping from their tips.

The dense slag sample produced at 1380° in run 3 was a dark dull glass, not easily broken. Its mineral content by X-ray diffraction was about 5% crystalline, mostly magnetite with some orthopyroxene. Crystals were seen in thin section embedded in the continuous glass phase. Other slag samples varied from totally glassy to predominantly crystalline.

The crystalline slag sample was found adhering to the bottom of the tap hole rim after period 4. (Period 4 temperatures apparently were barely sufficient for slag flow.) It had cooled much more slowly than would be typical of a slag product. Its predominant crystalline content resembled pyroxene, but the crystals were curved. Perhaps this chain-structure silicate was ordered in less than three dimensions.

Substantial amounts of unreacted quartz crystals were found by XRD in slag samples produced at the relatively low temperatures of period 4. A more reactive SiO_2-bearing mineral than quartz sand may offer conversion rate advantages at these lower slag temperatures. Other feed solids apparently fused and mixed well in all test conditions. Any unconverted pyrite or gypsum would have been detected by XRD.

SUMMARY OF REACTOR PERFORMANCE

Fuel should be in moderate excess for high SO_2 concentration and efficient slag desulfurization. 2 to 4 percent CO in product gas appears to be a suitable excess.

Reaction temperature around 1360°C appears to be sufficient for effective SO, production, efficient quartz reaction, and reliable slag drainage without damage to the refractory lining.

High reaction temperature apparently correlates with low-void, high-density slag.

A section was cut from the tap hole drip lip after period 4, and polished to examine the slag-refractory interface. The interface remained sharp, with no visible erosion or penetration of slag into refractory. However, electron microprobe showed 1 mm interpenetration on refractory test chips tested earlier in the tube furnace. The refractory appears durable, based on this limited 7-8 total hours contact with the melt.

Untreated phosphogypsum can leach acid and other undesirable elements into ground water, and it releases small amounts of radon to the air. Conversion into glassy slag virtually eliminates these effluents. Environmental characteristics of FLASC product slag are reported separately in this symposium.

CONCLUSIONS

Results so far support technical feasibility for entrained slagging reduction of phosphogypsum. Table 5 examines economic performance. Feed and product proportions were computed in the sample LYNX simulation in the Appendix. This preliminary projection considers only feed costs and product values. Capital cost and other operating costs are neglected, pending better data.

As environmental standards become more strict, there could be significant costs associated with conventional disposal in gypstacks. The gypsum cost in Table 5 then would become negative. Depending probably on standards for direct gamma exposure, FLASC slag may be approved for use as synthetic aggregate in concrete. A byproduct credit of $5 or more would result. Changes in either parameter would benefit process economics.

TABLE 5. Preliminary Economic Projection

FEEDS	UNIT VALUE	AMOUNT	COST
Gypsum, air-dried basis	0	100 tons	0
Natural gas	$3.20 KSCF	35 KSCF	111
Pyrite	$32/ton	16 tons	506
Coal, Midwestern high-sulfur	$25/ton	17 tons	430
Sand	$5/ton	1 ton	5
		TOTAL	1052
PRODUCTS			
Slag	0	61 tons	0
Sulfuric acid, 100% basis	$30/ton	70 tons	2108
		NET RETURN	1056

ACKNOWLEDGEMENTS

The authors wish to express their appreciation to the Florida Institute of Phosphate Research and the US Environmental Protection Agency for sponsoring this project.

APPENDIX
PROCESS SIMULATION WITH COMMERCIAL CONDITIONS BY LYNX PROGRAM

```
                    ==============================
                    I  FLASC PROCESS SIMULATION  I
                    ==============================

Inputs:                                         Time 12:46:18  06-03-90
-------
   REDRAT    PCTS    PCTF     PRESS    FERAT  FGRAT   SCALE
    .971  40.000  16.000      .956     .000    .050   4.000    .000
  GYPSUM    SAND  PYRITE      COAL     AIR  FUEL_GAS PROD_GAS SLAG   EXIT_GAS
    350.    350.     30.       30.     900.     25.   1500.   1330.    1200.
 DMMF  H       C       N         O       S     COAL COMPOSITION, MOLES/100G
   4.653   6.944    .109      .507    .071
    TIME  VOLUME COAL_HOF HEAT_COND
     1.5    60.0  -169.0       .0

RC(K,I) NUMBER OF MOLES OF COMPOUND K IN 100 GRAMS OF FEED MATERIAL I.
                      I=1         2          3          4          5          6
 K                  Gypsum     Sand       Pyrite     Coal       Air       FUEL GAS
 1  CaSO4          .54174     .00000     .00000     .01070     .00000     .00000
 2  CaSO4.5w       .00000     .00000     .00000     .00000     .00000     .00000
 3  SiO2           .40503    1.21238     .13297     .09177     .00000     .00000
 4  Ash            .01910     .27153     .02989     .03569     .00000     .00000
 5  FeS2           .00000     .00000     .71155     .06188     .00000     .00000
 6  FeS            .00000     .00000     .03819     .00000     .00000     .00000
 7  Water          .00000     .00000     .01670     .52995     .00000     .00000
 8  H2O vap        .00000     .00000     .00000     .00000     .05490     .00000
 9  N2             .00000     .00000     .00000     .00000    2.71323     .00000
10  O2             .00000     .00000     .00000     .00000     .71891     .00000
11  DMF coal       .00000     .00000     .00000     .72489     .00000     .00000
12  METHANE        .00000     .00000     .00000     .00000     .00000    6.23325

Outputs:
--------                  FEED AND PRODUCT STREAMS
                          ========================

                                      AMOUNT   ENTHALPY
                       I   STREAM    (grams)    (cal/g)
                       1   Gypsum    100.000    -2666.1
                       2   Sand        1.030    -2565.4
                       3   Pyrite     18.894     -600.4
                       4   Coal       20.581     -745.1
                       5   Air       182.015      198.6
                       6   FUEL GAS     .875    -1115.4
                       7   Prod gas  250.579     -352.8
                       8   Slag       72.818    -2367.2

                 MIXTURE SPECIFIC ENTHALPY (CAL/G) IS  -806.3


                            FEED SPECIES MOLES
                            ==================

  CaSO4          .5439        CaSO4.5w      .0000         SiO2            .4615
  Ash            .0349        FeS2          .1472         FeS             .0072
  Water          .1122        H2O vap       .0999         N2             4.9385
  O2            1.3085        DMF coal      .1492         METHANE         .0545
```

```
                          PRODUCT SPECIES MOLES
                          =====================
  H2             .0246          H2O            .6437          CO             .1547
  N2            4.9466          CO2            .9358          SO2            .8561
  CaSiO3         .2247          Ca2SiO4        .1596          Ca3SiO5        .0000
  Fe2SiO4        .0772          FeS            .0000          Ash            .0349


            DISTRIBUTION OF CHEMICAL ELEMENTS (MOLES/100G MIXTURE)
            ======================================================
              H       C       N       O       S       Si      Ca      Fe      Ash
Mixture     .4133   .3372  3.0592  1.8565   .2647   .1427   .1682   .0477   .0108
Gypsum      .0000   .0000   .0000  2.9770   .5417   .4050   .5417   .0000   .0191
Sand        .0000   .0000   .0000  2.4248   .0000  1.2124   .0000   .0000   .2715
Pyrite      .0334   .0000   .0000   .2826  1.4613   .1330   .0000   .7497   .0299
Coal       4.4328  5.0336   .0790  1.1238   .1861   .0918   .0107   .0619   .0357
Air         .1098   .0000  5.4265  1.4927   .0000   .0000   .0000   .0000   .0000
FUEL GAS24.9330  6.2332   .0000   .0000   .0000   .0000   .0000   .0000   .0000

% SO2 after gas is burned, dried and diluted to make SO3  9.30
% Oxygen in dry air 20.95
Foregoing data do not include fuel gas combustion offsetting heat conduction.


                         PRODUCT GAS VOLUME PERCENT
                         ==========================
                                     RAW      DRY
                         H2          .32      .36
                         H2O        8.51      .00
                         CO         2.05     2.24
                         N2        65.42    71.51
                         CO2       12.37    13.53
                         SO2       11.32    12.37


                       PROJECTED SLAG ANALYSIS, WT %
                       =============================

                           SiO2       38.08
                           CaO        41.89
                           FeO        15.23
                           Sulfide      .00
                       Balance is other oxides (ash)
```

CHARACTERISTICS OF BY-PRODUCT SLAG FROM PHOSPHOGYPSUM

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ABSTRACT

A process is being developed to recover sulfur dioxide from phosphogypsum by high temperature slagging reduction. Pulverized coal, gypsum powder, and pyrite are sprayed with air into a flame. SO_2 is released, and the particles fuse to form a free-flowing liquid. The melt drains into water where it quickly quenches, producing a nonporous, glassy slag. Based on favorable laboratory results, the "FLASC" program has advanced to pilot scale.

This report examines environmental characteristics of the byproduct slag. Measurements on laboratory slag samples are supplemented by projections to estimate slag leaching, radon emanation, and gamma ray activity.

Any sulfide present resists leaching at pH 4.0. Arsenic and lead leaching may exceed EPA standards, depending on feed pyrite quality. Radon emanation is expected never to be a significant hazard. Direct gamma activity may or may not be hazardous, depending on uranium content of parent phosphorite ore, and on yet-undecided environmental standards.

NOMENCLATURE

c_i	Trace element concentration in coal, PPM
g_i	Trace element concentration in phosphogypsum, PPM
p_i	Trace element concentration in pyrite, PPM
F_i	Leachate concentration from FLASC slag, PPM
f_i	Trace element concentration in FLASC slag, PPM
i	Trace element index
T_i	Leachate concentration from Texaco coal gasifier slag, PPM
t_i	Trace element conc. in Texaco coal gasifier slag,, PPM
v_i	Fraction distribution of volatile element i into product slag
R	Ratio of gamma radiation from radium and its daughters to gamma from U^{238}.

INTRODUCTION

Science Ventures is developing a process to recover sulfur dioxide from phosphogypsum for recycle into the wet phosacid process. Phosphogypsum powder is reduced with pulverized coal suspended in a flame. Condensed products melt and drain from the reactor, and a gas rich in SO_2 is produced. The process has been named FLASC for Flash Sulfur Cycle. Its technology and projected economics are described elsewhere in this symposium.

Conversion into slag reduces the weight by about 40%, and the volume by about 60% compared to untreated phosphogypsum. It may also overcome or greatly reduce groundwater leaching and radon emanation. EPA standards (which are undecided as of this writing) may permit use of the slag as synthetic aggregate in concrete, possibly depending on its gamma activity. Significant byproduct credits could result, while eliminating a major source of hazardous waste.

This report examines environmental characteristics of FLASC byproduct slag, including leaching, radon emanation and direct gamma activity. Estimates and correlations based on behavior of related materials are used to supplement available measurements. Slag trace element concentrations are computed from feed compositions.

SLAG COMPOSITION AND STRUCTURE

SOURCE AND PROPERTIES

A 2-liter laboratory reactor was built to physically simulate conditions expected of commercial process operation. A 60-liter pilot plant has also been completed, but has not produced slag as of this writing.

Molten slag drained from the laboratory reactor and fell into water, as would be the case in commercial processing. The slag particles are roughly round, nearly black lumps of glass. Hardness ranges from 5.5 to 6.5 on Mohs scale, which is comparable to ordinary glass or iron. X-ray diffraction shows the slag to be about 95% vitreous. The 5% crystalline content is primarily magnetite and pyroxenes. Thin section microscopy also shows the material to be mainly vitreous.

PHYSICAL STRUCTURE

Figure 1 is a scanning electron microscope photo of a *cut* slag drop. Figure 2 photo shows a thin section of another slag sample produced at relatively low temperature (1288-1320°C). The small jagged white patches are quartz grains remaining undissolved. Both pictures show larger spherical voids. These are formed by gas trapped in the melt at the moment of solidification.

Because the slag is produced in a molten and freely fluid state, any voids become closed gas bubbles due to surface tension. Unlike sintered materials, the slag lacks microscopic internal pores. Any crystalline phases present are embedded in the continuous glass phase, so that there are no diffusion paths at crystal grain boundaries. There is no externally-connected porosity.

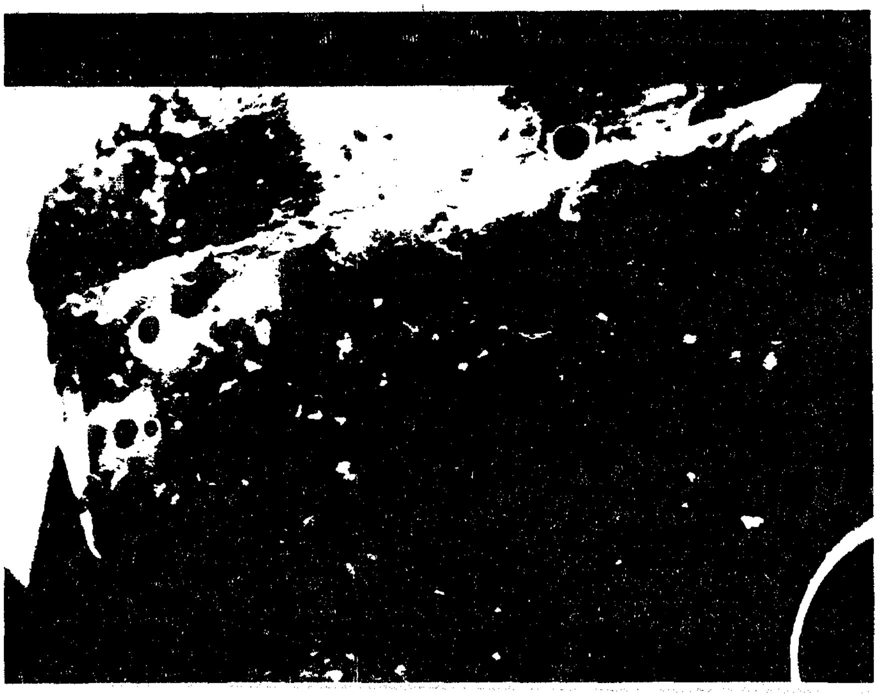

FIGURE 1. SEM photograph of a FLASC slag drop from period 4. Note spherical voids in the continuous glass phase. No crystals were detected in this sample. White tufts are artifacts of cutting.

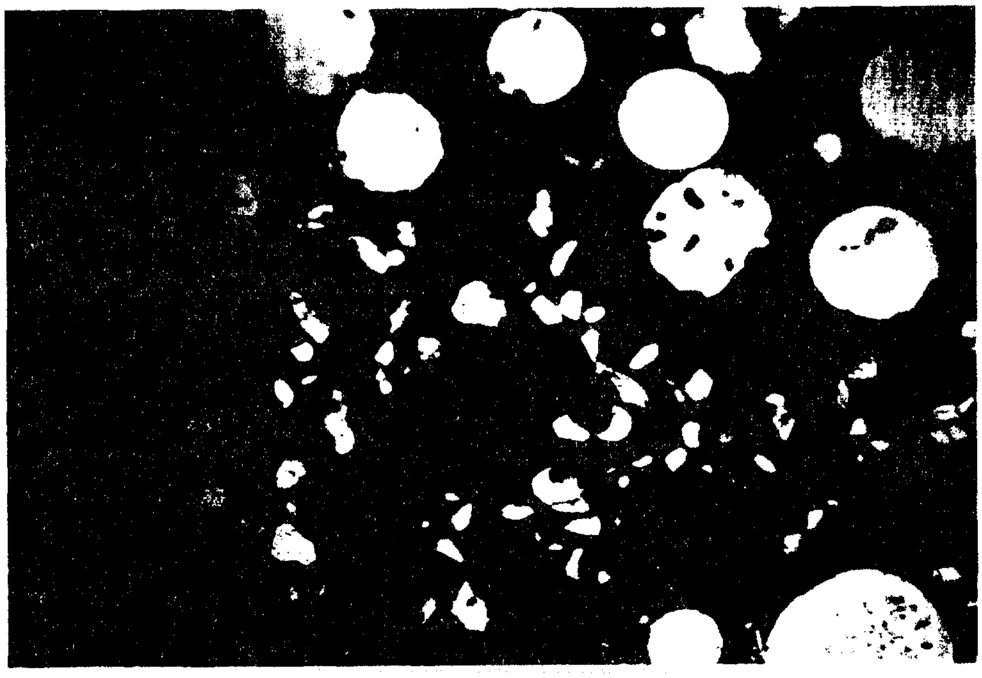

FIGURE 2. Slag thin section from period 4 seen by transmitted light. Small angular white patches are undissolved quartz grains embedded in glass phase. Larger spheres are gas bubbles.

FLASC slag produced in the lab reactor had about 1 cm mean particle diameter, and .00063 m^2/g surface to mass ratio, measured geometrically. Phosphogypsum surface/mass varies, but is roughly of order 1 m^2/g. Conversion into slag greatly reduces surface area available for leaching and radon emanation.

CHEMICAL COMPOSITION

The major oxide composition of the slag is given in Table 1. These proportions are roughly comparable to blast furnace slag, or elemental phosphorus slag. Trace elements in the slag have not been measured. They are estimated from analyses of typical FLASC feed materials in the next section.

Table 1. Major Oxide Composition of FLASC Slag

Oxide	Wt. Percent
CaO	41.9
SiO_2	38.1
FeO	15.2
P_2O_5	1.5
SO_3	1.0
Na,K,Mg,Ti, etc.	2.3

LEACHING

The leaching of toxic elements and acid into the environment is of concern for any waste material produced by industry. Phosphogypsum is sparingly soluble at 2.4 g/liter, while the slag is insoluble. Phosphogypsum has roughly 1000 times the surface area of slag made from it. Trace element leaching depends on surface area and solubility.

SULFIDE LEACHING TEST

Thermodynamic calculations indicate that a minor amount of sulfide will be produced under certain conditions in the FLASC reactor (Laird and Hanson, 1990). Two samples of slag known to contain sulfide were selected for sulfide leaching tests. One sample had been produced in the FLASC laboratory entrained reactor, and the other was prepared in a crucible in a controlled atmosphere furnace in strongly reducing conditions.

One-half gram samples were ground to pass 200 mesh. To simulate extremely acidic rain, 5 ml of pH 4.0 buffer solution was used to treat each pulverized sample for 48 hours in a sealed container. No detectable H_2S was released from either slag sample. The presence of sulfide was then verified by treatment with concentrated HCl.

TRACE ELEMENT LEACHING

The U. S. EPA considers the following elements to be toxic, and has set leaching standards: arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver. Copper, manganese and zinc have secondary drinking water standards. Other elements are included here for completeness.

Trace Elements in Slag

Table 2 contains data on trace elements present in FLASC slag. These values were calculated from the compositions of feeds used to make the slag, taking volatility into account. Analyses for the feeds are included, along with references for these typical composition data. The slag composition is then compared to leaching data for related vitreous coal slag, to identify elements most likely to be environmentally significant.

Trace element concentrations in slag are computed as follows:

$$f_i = 1.93v_i(.712g_i + .135p_i + .146c_i).$$

Concentrations in phosphogypsum, pyrite and coal are g_i, p_i and c_i respectively, all in PPM. The fraction of element i distributed into slag is v_i, and is 1.0 for nonvolatile elements. The typical feed/slag mass ratio is 1.93. The other coefficients are typical mass fractions in the feed mixture. About .7% sand used to adjust SiO_2 in feeds is neglected.

Table 2. Trace Element Content in FLASC Slag

Element i	Gypsum g(ppm)	Pyrite p(ppm)	Coal c(ppm)	FLASC Slag f(ppm)	Nonvol. Fract. v	Refs.		
Sb	0.2	150	1.05	5.7	0.145	e	f	b
As	0.85	750	15.8	70.9	0.354	e	f	a
Ba	10		81	36.6	1.000	e		c
Be	1		3	2.2	1.000	d		c
Cd	3		2.85	1.1	0.225	d		b
Cr	21		50	43.0	1.000	e		c
Co	0.58	350	3	92.5	1.000	e	f	c
Cu	8	350	24	108.6	1.000	e	f	c
Pb	9	1000	11	275.0	1.000	e	f	c
Mn	25	150	71	93.3	1.000	e	f	c
Hg	2.1		0.18	0.3	0.089	e		b
Mo	6.6		9.7	11.8	1.000	e		a
Ni	13	75	35	47.2	1.000	e	f	c
Ra	0.00002		0	0.00003	1.000	e		
Se	1.4	30	1.5	2.9	0.291	e	f	b
Ag	1.3	5	0.2	3.1	1.000	e	f	c
U	3		0.8	4.3	1.000	g		c
V	2.9	30	22	18.0	1.000	e	f	c
Zn	340	3000	124	1280.5	1.000	e	f	c

References to sources of the feed analyses are given by letters in three columns corresponding to gypsum, pyrite and coal.

a Baughman, 1978.
b Denchfield, et al, 1982.
C Coal Data Bank, U. Pennsylvania.
d May and Sweeney, 1984a
e May and Sweeney, 1984b
f Fleisher, 1955

The measure of volatility, v_i, has been determined for each of the volatile elements by using data from Denchfield, et al., 1982. That study investigated leaching of coarse slag from the Texaco coal gasifier.

The Texaco slag resembles FLASC slag in several ways. Like FLASC, it is produced from a high-speed entrained reaction at about 1315°C. The Texaco slag is also drained from the reactor in a completely molten and freely fluid state. Like FLASC, Texaco slag is quickly quenched by falling into water, where it forms glassy lumps of similar particle size. However, Texaco conditions are more strongly reducing than FLASC, and Texaco slag is richer in SiO_2 and Al_2O_3.

Leaching Estimation Method

Leaching tests on the Texaco slag were performed according to U.S. EPA standards (Federal Register, 1980). A 100 gram sample is treated with 16 times its weight of deionized water, adjusted and continuously monitored to pH 5.0 with acetic acid. After 24 hours agitation the solution is filtered, diluted to 2 liters, and analyzed for toxic metals. Acceptable limits are 100 times the EPA Interim Primary Drinking Water Standards, as listed in Table 3.

Projected Leaching

FLASC slag leaching in Table 3 is estimated from the Texaco leaching results and relative trace element concentrations in FLASC and Texaco slags:

$$F_i = f_i T_i / t_i$$

T_i and t_i are concentrations in PPM of element i in Texaco leachate and slag respectively (Denchfield, et al, 1982).

ENVIRONMENTALLY SIGNIFICANT LEACHATES

Values in Table 3 are all within environmental standards. However, the margin is not great for arsenic and lead, which originate primarily with pyrite. These trace elements are highly variable in pyrite. Up to 50,000 PPM lead and 5,000 PPM arsenic were found in a worldwide survey of pyrite analyses (Fleisher, 1955).

Lead and arsenic leaching could easily exceed standards with impure pyrite feeds. FLASC feed materials must be selected accordingly.

RADON EMANATION

Natural uranium 238 replaces some of the calcium atoms in apatite, and typically amounts to 100-200 PPM in US phosphate ores (Habashi 1970). U^{238} decays with 4.5 billion year half life according to the decay series in Figure 1. After fourteen steps, stable lead 206 is produced. Undisturbed phosphate ore contains each of the active daughter products in radioactive equilibrium with U^{238}. That is, each active species decays at the same count rate regardless of its half life. (This equilibrium is approximate due to minor radon losses.)

Table 3. Trace Element Leaching from FLASC Slag

Element i	FLASC Slag f(ppm)	Leachate F(ppm)	EPA Max. (ppm)
Sb	5.7	0.44	
As	70.9	0.84	5
Ba	36.6	0.0015	100
Be	2.2	0.0017	
Cd	1.1	0.0025	1
Cr	43.0	0.0003	5
Co	92.5	0.011	
Cu	108.6	0.027	100
Pb	275.0	0.98	5
Mn	93.3	0.0059	5
Hg	0.3	0.0002	0.2
Mo	11.8	0.036	
Ni	47.2	0.022	
Ra	.00003		
Se	2.9	0.031	1
Ag	3.1	0.33	5
U	4.3		
V	18.0	0.024	
Zn	1280.5	4.38	500

When phosphoric acid is extracted from the ore, radioactive daughter species are separated, disturbing the equilibrium. Over 90% of the uranium dissolves, and becomes part of the fertilizer (May and Sweeney 1980). Thorium and lead also dissolve, but radium and polonium sulfates are insoluble and become part of the phosphogypsum waste. Thus, the principal nuclides in phosphogypsum and FLASC slag include Ra^{226} and the isotopes below it in Figure 3.

Radium decays with 1620 year half life to radon 222, which is an inert gas. This is considered the principal health hazard, because radon and its daughters can be inhaled and retained in the lungs. Alpha emissions in lung tissue pose a cancer risk. Gamma ray emissions associated with some of the decays in Figure 1 are considered a lesser hazard. US phosphogypsum waste contains typically 15-25 pCi/g of radium 226, depending on the uranium content of the parent phosphate ore (Medora and Trefler 1988, May and Sweeney 1980).

MEASURED RADON EMANATION

Radon produced from FLASC slag was compared to radon produced from an equivalent amount of the phosphogypsum that had been used to make the slag. The radon was collected by adsorption on activated charcoal. Activity of the charcoal was then measured by gamma spectrometry, and results evaluated statistically.

Sample Preparation and Activity Measurement

Various samples of laboratory slag were sealed in bags made from open-weave nylon, which were labeled to retain their identity. 80% of the slag tested was highly vitreous (quickly cooled) material.

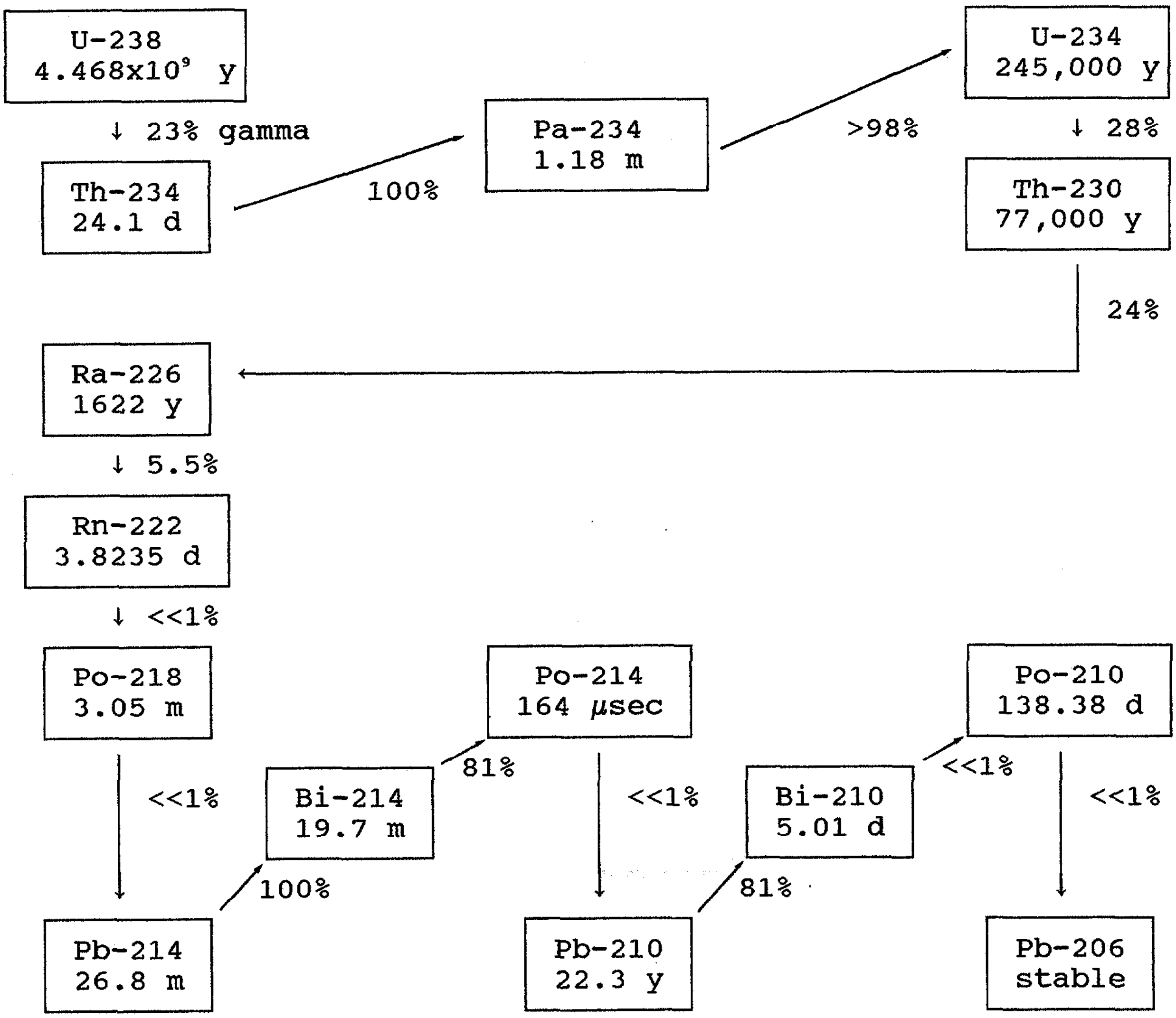

FIGURE 3. Uranium-238 to Lead-206 Decay Series

Downward steps indicate alpha particle emissions. Diagonal steps are beta emissions. Percentages shown with each decay represent the fraction of decays producing a gamma ray.

This is expected to be most representative of a commercial product. About 20% of the slag tested was a more slowly cooled and predominantly crystalline sample collected from just below the tap hole after one of the runs.

The combined slag sample weighed 96.08 grams. It was compared to the phosphogypsum that had been used to make it. 119.2 grams of gypsum was calculated from composition data to match molar calcium and radium content of the slag. The particle sizes of slag and phosphogypsum were not altered. Slag had a mean particle diameter of about 1.0 cm. It was nearly black and generally shiny.

Charcoal cartridges supplied by an EPA-recognized testing laboratory (Radon Testing Services of San Diego) were placed upside down on the test materials for easy radon transfer. The test materials, along with the charcoal cartridges, were sealed inside 5-cup plastic containers for 46 hours and 20 min. The containers were sealed outdoors to avoid any radon from the building. Exposed charcoal cartridges were promptly sealed airtight after removal.

Activity Measurement

Sample and background gamma activities were counted later the same day using a lead shielded scintillation counter with NaI crystal detector. To minimize background, only the energy range from 280 to 620 KEV was counted.

A cartridge from the same manufacturer's lot as the sample cartridges was used to measure background. The two sample cartridges were also counted before exposure to verify that they were the same at that time. The testing laboratory was not told which sample cartridge was which.

Results are shown in table 4 along with the statistical variance of each. According to these figures, slag releases 0.039 as much radon as untreated phosphogypsum would release. If gypsum has typically 14% emanation power (Pensko et al 1980, Ackers et al 1985), emanation power of the slag would be 0.5% of radium decays.

Table 4. Gamma Activity Measurements

	COUNTS		VARIANCE	
Sample	Gross	Net	Gross	Net
Background	2085	0	2085	-
Slag	2104	19	2104	4189
Phosphogypsum	2567	482	2567	4652

Statistical Analysis

Because there is no covariance between net counts, it is proper to use the standard formula for propagation of error. A standard deviation of 0.134 is thereby computed in relative units of slag/gypsum emanation, compared with the mean value 0.039.

This measurement is encouraging but imprecise. To reduce the error bounds, the counting time must be extended. The 1-sigma range of uncertainty with these data is 0-.173 for slag/gypsum relative emanation, or 0-2.4% emanation power.

PROJECTED RADON EMANATION

The emanation behavior of related materials is discussed below, and is used to estimate slag emanation based on its physical structure.

Radon Emanation Mechanism

When a radium atom decays, a high-speed alpha particle is emitted and radon recoils in the other direction with 101 KEV kinetic energy. If the decay occurs within about 3×10^{-6} cm of an external surface or an intraparticle pore or crevice, the newly formed radon ion may have sufficient momentum to escape the mineral (Tanner 1964, Andrews and Wood 1972). The ion is likely to re-embed itself if another solid surface is within .001 cm. Otherwise it can diffuse away and ultimately enter the air or water. Any moisture in pores absorbs kinetic energy, making the radon less likely to re-embed itself in solid, and more likely to escape.

Gas Retention in Minerals

If the trajectory ends in solid mineral, radon is trapped until it decays to polonium. Diffusion coefficients in minerals at 25^0C are $\le 10^{-21}$ cm^2/sec, so that gases are retained for geologically long times (Tanner 1964, Wilkening 1974).

This is the basis of potassium-argon dating of volcanic rocks. Like radon, argon is an inert gas. Also like radon, argon 40 forms as a decay product (of radioactive potassium 40). By comparing Ar^{40} to K^{40} content, the age of a rock can be measured. Vitreous and crystalline minerals retain the gas for billions of years, so that rocks as old as the earth can be dated (Faure, 1986, Funkhouser 1968, Dalrymple 1968).

Radon Emanation in Relation to Surface Area

Studies (Burnett, et al, 1988) on crushed granite and phosphate ore have found that radon emanation is governed principally by radium content and effective BET surface area. (BET surface area, after Brunauer, Emmet and Teller, is a measurement of externally-connected internal surface area based on gas adsorption.)

Based on Burnett's measurements, the ratio of emanating power (percent of radium decays) to surface/mass ratio (m^2/g) is 0.19 for dry phosphate ores. Applying this to the FLASC slag surface/mass ratio, 0.00012 percent emanation power is predicted.

Blast furnace slag emanation power ranges from 0.31 to 0.62% (Pensko et al 1980, Paredes et al 1987). Mineral wool insulation made from Tennessee elemental phosphorous slag had emanation power of .47% in spite of its relatively large surface (Paredes 1987).

Elemental Phosphorus Slags

Elemental phosphorous is produced in electric furnaces under strongly reducing conditions, with silica and iron added as fluxes. This vitreous calcium-iron silicate is probably the most closely related to FLASC slag. Table 5 contains emanation coefficients for elemental phosphorus slags, as well as their phosphate ores (Paredes 1987). Phosphogypsum is included for comparison.

Table 5. Emanation Power of Phosphate Slags and Ores

Material	Percent Emanation
Florida Phosphate Slag	.25
Tennessee Phosphate Slag	.13±.021
Montana Phosphate Slag, expanded	.064
Tennessee Phosphate Ore	3.8
Montana Phosphate Ore	2.1
Typical Phosphogypsum	14.

Emanation from these elemental phosphate slags is about 3% of that of their ores, or about 1% that of phosphogypsum.

Radon exhalation from Montana and Idaho phosphate slag was also evaluated by Montana State Health Department (Lloyd 1983). Emanation coefficients were not computed, but the slags were found to release 0.47% to 0.88% as much radon as their parent ores. Those slags were deemed not to pose a radon hazard, although direct gamma could be hazardous particularly from the Idaho slags.

Projected Radon Hazard

Based on the foregoing comparisons to phosphorus slags and other related materials, we estimate that FLASC slag would release not more than 1% as much radon as the phosphogypsum it is made from. This is consistent with the measured value of 3.4%, but is more probable due to error bounds of the measurement. The resulting health hazard can be evaluated by comparison with phosphogypsum radon hazards.

A test house was built with all its wall panels cast from concrete containing 50% Florida phosphogypsum (Chang 1987, Medora and Trefler 1986). Gypsum in the walls contained 20-25 pCi/g of radium. The house was sealed and unventilated for worst-case conditions. Soil radon was excluded by leaving a 76 cm open space below the house. After 8 days, radon working levels as high as .048 were measured.

As yet there is no uniform EPA standard for radon exposure. Probably the strictest limit suggested is in the EPA recommendations to Florida (1979) for new home construction, of .009 Working Level (Guimond 1985). If the test house above had FLASC slag in place of phosphogypsum in its walls, the estimated radon concentration would be .0005 WL. It is therefore unlikely that FLASC slag radon will pose a significant health hazard, even in worst case conditions.

GAMMA RADIATION

Aside from the possibility of airborne radon, there may be health hazards due to gamma radiation from isotopes in the slag. FLASC slag differs from elemental phosphorus slags in its gamma potential. Essentially all isotopes above Ra^{226} in the decay series are separated in the wet phosacid process, whereas those isotopes remain with the elemental phosphorus slags. FLASC gamma activity (counts/sec) is thereby reduced by about 50%, other things being equal.

This section evaluates FLASC slag gamma activity based on its radium content. Essentially all of the phosphogypsum radium is retained when it is converted into slag. Phosphogypsum radium content in turn depends on uranium concentration in the ore concentrate used to make it.

ESTIMATION METHOD

The following analysis assumes equilibrium among all the daughters of radium. This is a worst case assumption, because many years are required for ingrowth of long-lived lead 210.

Nuclides are concentrated in the slag due to its 40% reduction in mass compared with phosphogypsum. A further concentration results from retention of the 14% of radon that typically would escape phosphogypsum. Together, these factors yield a factor of 1.9 increase in slag gamma activity compared to air-dry gypsum. Gamma attenuation due to iron in the slag is neglected.

Decay series information is used to relate slag activity to activity of the parent ore. For each decay step, there is a percentage of decays producing a gamma photon, shown in Figure 3. By summing these gamma percentages and assuming radioactive equilibrium, an activity ratio, R is computed for (Ra^{226} plus progeny)/U^{238}.

$$R = 268/23 = 11.7$$

Uranium 238 gamma activity in turn can be related to its concentration in ore according to its half life. For each PPM of uranium in the ore, there are .0124 U^{238} decays/sec, producing a gamma activity of .0773 pCi/g. Multiplying these values, a gamma activity of .905 pCi/g from radium and progeny is computed for each PPM of uranium.

To complete the analysis, another scale factor is needed to relate activity in FLASC slag to activity in ores. Calcium oxide typically constitutes 25% of the ore (Wilemon and Scheiner 1987). Ore-derived CaO typically constitutes 42% of FLASC slag. Since radium follows calcium to the slag, radium will be concentrated by a factor of 42/25=1.7 compared to the ore. Thus, each PPM of ore uranium leads to 1.5 pCi/g gamma activity in the slag. Since radium and its progeny account for half of the gamma activity of the ore, the slag will exhibit 75% as much total pCi/g as natural phosphate rock.

PROJECTED SLAG ACTIVITY

US phosphate ores range from 8 to 399 PPM uranium (Andrews and Bibb 1982) with South Carolina producing the highest, and Tennessee the lowest amounts. A typical range for Florida ore is 100-200 PPM (Habashi 1970). This leads to projected maximum slag activity range from 12 to 600 pCi/g, or a typical range from 150 to 300.

This is total gamma counts; not to be confused with pCi/g of radium. The radium contribution is much less.

Comparison with phosphate ore and phosphogypsum shows that FLASC slag is comparable in activity to both. Hazards due to direct gamma activity depend principally on uranium content of the ore, which is highly variable.

CONCLUSIONS

Leaching of most trace elements should never exceed EPA standards with FLASC feeds in a normal range of composition. The leachates most likely to exceed standards are lead and arsenic, which depend principally on feed pyrite quality.

Radon emanation has been both measured and estimated by correlation to related materials. Both results are that radon is never expected to present a health hazard, even for the worst case situation of an unventilated house built from FLASC slag.

Direct gamma radiation from the slag depends on uranium content of its parent ore. Total slag gamma activity is estimated to be about 75% of that of the parent ore, or 1.9 times that of phosphogypsum. Variations in processing conditions are expected to contribute little to variation in slag activity. The principal parameter affecting slag activity is uranium content of the ore, which varies by as much as a factor of 50 in the US. It is likely that some slags will exceed standards (when they are defined) and others will not.

When larger slag samples become available, these conclusions should be verified by more direct testing.

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"BENEFICIATION OF PHOSPHOGYPSUM FOR UTILISATION AS A SUPERIOR FILLER IN THE INDUSTRY".

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ABSTRACT:

This paper describes a phosphogypsum processing development in laboratory and pilot plant to attain sufficient purity for use as a mineral filler in the paper industry.

Research made by SERRANA S.A. DE MINERAÇÃO, Jacupiranga, Brazil showed that it is possible to remove impurities (silicates, oxides, etc) and to improve particles size distribution with a process that includes wet classification, desliming, froth flotation, screening and magnetic separation as main operations.

Serrana's phosphogypsum is the by-product (600.000t/yr) of a Fisons phosphoric acid process that uses apatite from a carbonatite - igneous phosphate rock.

At the present, this by-product is dumped, stored and used only as cement retarder and for soil amendment (240.000 t/yr).

The project for the new application as filler is in a very promising stage and on behalf of economic and environmental views it is quite interesting.

Laboratory and industrial tests of manufacturing printing and writing papers showed that is possible to increase the percentage level of the new filler, increasing the whiteness and mechanical properties of the final paper.

INTRODUCTION

Serrana is a company associated to the Brazilian Santista Group, whose activities were the production of phosphate raw materials for fertilizers. Along its expansion, Serrana developed the integrated utilisation of the ore, broadening its field of activities to cement and fertilizar production until reaching at its present stage what we call the Jacupiranga Idustrial Complex.

The mining activities of Serrana started 40 years ago at "Morro da Mina" in Jacupiranga, located in "Vale do Ribeira", São Paulo State (FIGURE 1). The "Morro da Mina" at that time at an elevation of 220 meters above sea level, contained a rich apatite ore, originated by deep weathering of a carbonatite during millions of years. Its grade was up to 20% P2O5. This ore called "residual" was concentrated in simplified stages of disaggregation, washing and magnetic separation.

More detailed geological studies, unfortunately, showed that the initial characteristics of the carbonatite did not extend to great depth. During the 60's Serrana engineers developed a process technology for concentrating from unique carbonatic ore by flotation.

In, 1969 the new plant went on stream demostrating the effectiveness of the newly developed process. A phosphate concentrate was produced by flotation of apatite and depression of carbonates thus enabling economic processing of a low grade (5% P2O5) phosphate ore, considered unecomic so far.

Modifications in the grinding circuit and the development of a specific Serrana flotation cell are examples of continuous technology research during the last 20 years wich allowed increase of apatite production capacity and an increase of apatite recovery from 65% to the present 73%.

In 1972, a cement plant was built which use the carbonate sub-products of the phosphate processing plant as principal raw material.

In 1974, the fertilizer Chemical Complex operated by Quimbrasil Química Industrial Brasileira S.A. was started.

Since 1987, the Jacupiranga Industrial Complex became a fully integrated phosphoric industry, including production of food-grade phosphoric acid as well as techinical grade for refined industries; both products have so far been imported. TABLE 1 shows the capacities of production units and FIGURE 1 shows the simplified flow chart of the Jacupiranga Industrial Complex.

3. RAW PHOSPHOGYPSUM PRODUCTION

In the Chemical Complex, phosphoric acid is produced by Fisons wet process. Phosphogypsum or calcium sulfate is the main by-product from the phosphoric acid plant and it is obtained as the following simplified reaction:

$Ca_5(PO_4)_3F$	+	H_2SO_4	+	$H_2O \longrightarrow$	H_3PO_4	+	$CaSO_4 \cdot 2H_2O$	+	HF
Apatite		Sulphuric acid		water	phosphoric acid		phosphogypsum		fluoridric acid

For a long time this by-product has been dumped and used only as cement retarder and for soil amendment.

Another project of a plasterboard plant is also being developed with very good results.

TABLE 2 presents the production and applications of Quimbrasil phosphogypsum, before use in the paper industry.

The disposal of phosphogypsum is costly and it is an environmental problem all over the world.

4. PROCESS DEVELOPMENT

The so-obtained phosphogypsum from phosphoric acid plant contains some impurities that result in problems for the paper industry.

Depending on the geological origin of the phosphate rock and on the phosphoric acid process there are different type and quantity of impurities and particles size. Coloured and oversize particles harm aesthetically and print quality, hard abrasive particles damage paper-making and printing presses with disastrous consequenses.

Jacupiranga phosphate rock occurs in an ore that consists of calcitic to dolomitic carbonatite with varying amounts of apatite, calcite, dolomite, magnetite, phogopite (mica), olivine and sulphides.

TABLE 3 presents the average mineralogical composition of the carbonatite and TABLE 4 the respective chemical analysis.

After milling, the phosphate concentrate obtained presents mineralogical and chemical compositions showed in TABLES 5 and 6, respectively.

As we can see, the apatite concentrate still presents amounts of calcite, magnetite and phlogopite.

After reacting this apatite concentrate with sulphuric acid in the phosphoric acid process, the formed phosphogypsum still contains the insoluble impurities, mainly phlogopite, magnetite and unreacted apatite.

Mineralogical and chemical analysis of raw phosphogypsum are shown in TABLES 7 and 8.

The main impurities and consequent problems that they cause in the paper occur are shown in TABLE 9.

Although the presence of some impurities, Quimbrasil's phosphogypsum has the great advantage that it is its high brightness (88% - Photovolt measure) as an extremelly white mineral.

Particles size distribution of raw phosphogypsum is showed in FIGURE 3.

In FIGURE 4 it is shown the crystals shape of phosphogypsum and impurities.

The process development to attain sufficient purity of phosphogypsum for use as mineral filler in the paper industry was carried out in laboratory and pilot plant scales.

For each tested processing route it was generated a sample that was used in laboratory manufacturing papers to be appreciated for the paper industry.

With this procedure, it was possible to reach in the laboratory an acceptable product (10th. product) as indicated in FIGURE 5.

TABLE 10 presents the comparison between control analysis of raw and pure phosphogyspsum (1st. and 10th product)

FIGURE 6 presents a picture of pure phosphogypsum and FIGURE 7 shows its particles size distribuition.

5. PILOT PLANT OPERATION

Since accepted the product to use as filler in printing and writing papers, we started running a pilot plant with 0,6 t/h feed capacity and we tested during one year, 9 circuit variations as indicated in TABLE 11.

Each sample produced by the 9 circuits was submited to acceptance.

Sample produced in the seventh circuit was accepted and the first industrial test in a paper machine was done with 10 tons of this product.

Once aproved in the industrial test we started operating a pilot with initial production capacity of 150 t/month.

FIGURE 8 shows the Pilot Plant production since June to October, 1989.

PROCESS DESCRIPTION

CLASSIFICATION: 2 Stages with Flat-bottomed hidrocyclones of 4 inches diameter.

DESLIMING: 2 Stages with Conical hidrocyclone of 40mm diameter.

FLOTATION: The flotation of phlogopite is carried out between pH 3,0 and 5,0 in rougher and scavenger stages.

The deslimed phosphogypsum is conditioned with 20 to 40g/t of etheraminacetates during 3 minutes.

It is not necessary a frother dosage.

SCREENING: To eliminate eventual coarse mica and process impurities.

HIGH INTENSITY MAGNETIC SEPARATION: To remove fine magnetite.

THICKENING: To reduce water content to feed the filter.

FILTERING: To obtain 30% of moisture content in final product.

The pure phosphogypsum produced in this process has been sold for information papers (magazines, business and writing applications) and for packaging and wrapping papers since July, 1989.

6. CHARACTERISTICS OF PAPER MADE WITH PURE PHOSPHOGYPSUM.

The reasons for mineral filler usage in the paper industry are: to reduce costs substituting part of fiber, to improve paper properties and to aid paper processing.

Laboratory tests filled with pure phosphogypsum in different percentage levels comparing with kaolin are presented in TABLE 12. Very important advantages have comproved with its utilization:

- Done to its shape, phosphogypsum crystals fill bettor the voids between fibers and ease drainage and pressing, reducing drying energy, and raising both paper machine speed an productivity.
- Phosphogypsum has a very good compatibility in the paper because the crystals are markedly acicular like natural fibers. So this filler gives the sheet a more uniform formation and homogeneous distribution throughout paper structure FIGURES 9 and 10.
- It improves mechanical properties and allows to increase percentage level of filler.
- Because its high brightness it is possible to reduce chemical reagents used in the paper machine to increase whiteness.
- Phosphogypsum is a low cost raw material.

7. MARKET OUTLOOK

Phosphogypsum production capacity in Brazil is about 3,3 million tons/year. Serrana/Quimbrasil participante with 600,000 tons/year of this total amount. Opposite to Quimbrasil, the reamaining national phosphoric acid producers have a lower quality phosphate ore that results in raw phosphogypsum with pronunced quantity of impurities - some of which radioactive - dark colors (beige to brown). These characteristics invalidate its application as mineral filler for writing and business papers. These kinds of paper represent the biggest demand for noble mineral filler.

Brazilian paper industry produced 4,683 million tons last year that means about 500,000 tons of mineral filler, mainly kaolin followed in consumption by calcium carbonate. The outlook for the 2000 year foresees a duplication in paper production and consequently increase in mineral fillers consuption.

Southeast region, where Serrana/Quimbrasil is located should share about 40% of Brazilian demand that represents an expecting annual consumption of 400,000 tons of filler.

Huge territory extension associated with railway transportation deficiencies result in road transportation with high costs to the production outflow. This fact benefits the regionalization of raw material demand for the paper industry.

Main kaolin and natural gypsite deposits are located in northern and northeast regions that will benefit the compatitivity in relation to Quimbrasil´s pure phosphogypsum costs. Another advantage is the pure phosphogypsum excellent quality and performance in the paper industry.

Done to its high purity and quality it is expected an usage diversification in paints, rubber, plastics, cosmetics, insecticides and pharmaceutical industries.

This may, the outlook for the market growth in medium and long terms are highly favourable.

8. INDUSTRIAL PLANT PROJECT.

Viewing to attain the market of mineral filler, mainly from the South region, which corresponds to the supply of the customer unities from an average distance of 800 Kms, one elaborated a basic project of a phosphogypsum processing industrial plant with capacity of 120,000 tons/year of pure phosphogypsum. It is forecast the location of this unity at the Quimbrasil Phosphoric Plant neighborhood, where the phosphogypsum by-product is unloaded, in order to reduce, this way, handling and transportation costs of the raw material.

The final product will present an average moisture content of 20 to 30% to be bagged in 1,5 tons containers (big-bag) order to avoid contaminations.

It is estimated an investment of US$ 10 millions for the implantation of this plant, considering that all of the basic infra-structure will be absorbed from the Jacupiranga Industrial Complex.

The total mass recovery of the process should be around 30%, with the approximate generation of 180,000 of tailing per year, which will be reused for the utilization as a cement retarder.

A dam system with recirculation of 80% of water will withhold the discharge and will assure the attainment of the environmental control rules.

The industrial plantstart-up planned for the beginning of 1991, though in this period the semi-industrial unity is operating for the supply of big volumes for tests and adequation of the customer's industrial installations from this new mineral filler.

9. SUMMARY AND CONCLUSIONS

The beneficiation process of phosphogypsum was studied and developed with the objective of producing a refined or pure phosphogypsum to use as mineral filler in the paper industry.

Brazilian paper mills have produced papers used in, for example magazines, business, writing, wrapping and packaging applications with excellent results.

Studies and tests have been made to use pure phosphogypsum in paper mineral coating as well as filler in paint, plastic, rubber, insecticides, cosmetic and pharmaceutical.

A new semi-industrial plant with production capacity of 30.000 t/year is operating since March, 1990. It will run to supply some paper mills until the start-up of the industrial plant with production capacity of 120.000 t/year, a 10 million dollars project.

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TABLE 1. JACUPIRANGA INDSUTRIAL COMPLEX PRODUCTION CAPACITIES.

	T/YEAR
MINING	
Ore	5,000,000
Waste	5,000,000
Mine Total	10,000,000
MILLING	
Phosphate Concentrate	500,000
CEMENT PLANT	
Cement Production	1.000,000
CHEMICAL COMPLEX	
Sulphuric Acid	245,000
Phosphoric Acid	150,000
Superphosphate SST/TSP	200,000
Monoamonium Phosphate	160,000
Food Grade Phosphoric Acid	25,000
Raw Phosphogypsum	600,000

TABLE 2. PRODUCTION AND APPLICATION OF QUIMBRASIL PHOSPHOGYPSUM.

	T/YEAR	%
Production	600,000	100
Cement Additive	180,000	30
Soil Amendment	60,000	10
Storage	360,000	60

TABLE 3. AVERAGE MINERALOGICAL COMPOSITION OF THE CARBONATITE

MINERALS	%
Apatite	12
Calcite	57
Dolomite	21
Magnetite	7
Phlogopite	2
Others	1

TABLE 4. AVERAGE CHEMICAL ANALYSIS OF THE CARBONATITE

P_2O_5	-	5%
CaO	-	49%
MgO	-	4%
SiO_2	-	1%
Fe_2O_3	-	6%
I. LOSS	-	34%
Others	-	1%

TABLE 5. AVERAGE MINERALOGICAL COMPOSITION OF THE APATITE CONCENTRATE.

MINERALS	%
Apatite	86
Calcite	7
Dolomite	3
Magnetite	0,5
Phlogopite	3
Others	0,5

TABLE 6. AVERAGE CHEMICAL ANALYSIS OF THE APATITE CONCENTRATE.

P_2O_5	–	35,5%
CaO	–	52,5%
MgO	–	1,4%
Al_2O_3	–	0,2%
SiO_2	–	0,4%
K_2O	–	0,2%
Na_2O	–	0,2%
Fe_2O_3	–	0,5%
F	–	1,4%
I. LOSS	–	6,8%

TABLE 7. AVERAGE MINERALOGICAL COMPOSITION OF RAW PHOSPHOGYPSUM.

Di-hydrate Calcium Sulfate	–	95,0%
Himi-Hydrate Calcium Sulfate	–	1,2%
Phlogopite	–	1,7%
Magnetite	–	0,5%
Apatite	–	1,4%
Others	–	0,2%

TABLE 8. AVERAGE CHEMICAL ANALYSIS OF RAW PHOSPHOGYPSUM.

P_2O_5	–	0,73%
CaO	–	32,95%
MgO	–	0,44%
Al_2O_3	–	0,26%
SiO_2	–	0,77%
K_2O	–	0,12%
Na_2O	–	0,05%
Fe_2O_3	–	0,10%
F	–	1,10%
I. LOSS	–	10,4%

TABLE 9. IMPURITIES IN RAW PHOSPHOGYPSUM , TYPICAL PROBLEMS THEY CAUSE IN THE PAPER AND THEIR CONTROL ANALYSIS.

IMPURITIES	PROBLEMS IN THE PAPER	CONTROL ANALYSIS
Mica (phlogopite) $(KMg_3Si_3Al_1O_{10}(F,OH)_2$	Bright and reflective points	K_2O
Magnetite	Back points, rugged areas formation and high abrasivity	Fe_2O_3
Apatite $(Ca_5\ (PO_4)_3F)$	Rugged areas and abrasivity	P_2O_5

TABLE 10. COMPARISON BETWEEN RAW AND PURE PHOSPHOGYPSUM.

PRODUCTS	CHEMICAL ANALYSIS (%)					
	P_2O_5	K_2O	MgO	Fe_2O_3	BRIGHTNESS (ELREPHO)	MASS RECOV.
1st	0,86	0,10	0,30	0,06	83	100
10th	0,58	0,007	0,02	0,02	90	50

PRODUCTIS CHARACTERISTICS

1st PRODUCT - By-product of phosphoric acid plant without any beneficiation, raw phosphogypsum.

10th PRODUCT - Phosphogypsum concentrate or pure phosphogypsum, this product was accepted in the paper industry.

TABLE 11. PILOT PLANT CIRCUITS TESTED.

CIRCUIT	CLASSIFICATION	DESLIMING	REVERSE FLOTATION	SCREENING	MAGNETIC SEPARATION	TOTAL MASS RECOVERY (%)
1	DSM Screen 150# (70)	-	Rougher (85)	-	Low Intensity (99)	59
2	-	Conical Hydrocyclone (95)	Rougher + Scavenger	-	Low Intensity (99)	66
3	Conical Hydrocyclone (55)	Conical Hydrocyclone	Rougher (85)	-	Low Intensity (99)	44
4	Conical Hydrocyclone (55)	Conical Hydrocyclone (95)	Rougher + Scavenger (69,5)	-	Low Intensity (99)	36
5	Flat-Bottomed Cyclone (65)	Conical Hydrocyclone (95)	Rougher + Scavenger (64)	-	Low Intensity (99)	39
6	Flat-Bottomed Cyclone (65)	Conical Hydrocyclone (95)	Rougher + Scavenger (64)	-	High Intensity (98)	39
* 7	Flat-Bottomed Cyclone (65)	Conical Hydrocyclone (95)	Rougher + Scavenger (69,5)	DSM Screen 150# (70)	High Intensity (98)	29
8	Flat-Bottomed Cyclone (65)	Conical Hydrocyclone (95)	Rougher (85)	DSM Screen 150# (70)	High Intensity (98)	36
9	Flat-Bottomed Cyclone (65)	Conical Hydrocyclone (95)	Rougher (85)	DSM Screen 100#	High Intensity (98)	41

(*) Accepted product.

TABLE 12. LABORATORY TESTS COMPARING PAPERS WITH KAOLIN AND PURE PHOSPHOGYPSUM.

PARAMETERS		MINERAL FILLERS				
		KAOLIN	PURE PHOSPHOGYPSUM			
PULP (CELLULOSE FIBER), g		50	60	80	90	60
FILLER, g		20	24	40	60	90
PERCENTAGE OF FILLER, %		40	40	50	67	150
PULP DRAINAGE RESISTANCE, SR		43	43	27	41	43
GRAMMAGE, g/m2		60,2	61,7	59,2	53,4	53,3
THICKNESS, mm		0,083	0,091	0,098	0,080	0,079
SPECIFIC VOLUME, cm3/g		1,38	1,47	1,66	1,50	1,47
TENSILE INDEX, Nm/g	L	56,5	65,7	49,8	53,8	29,4
	T	19,8	26,6	19,3	23,5	13,2
ELONGATION, %	L	2,8	3,0	2,0	1,8	1,8
	T	2,8	2,9	2,7	2,5	-
TEAR INDEX, mN . m/g	L	3,11	3,43	4,45	5,53	2,45
	T	6,61	5,97	6,46	6,47	4,49
COBB (WATER ABSORBENCY), g/m2		12,2	27,4	18,8	20,0	12,0
BRIGHTNESS, % ELREPHO		80,2	83,6	84,5	81,8	84,3
OPACITY, % ELREPHO		88,1	83,3	81,7	77,4	80,1
SCATTERING COEFICIENT, m2/kg		54,9	43,3	43,7	37,3	42,7
ASHES, %		23,2	20,5	17,0	25,0	45,8

L - LONGITUDINAL
T - TRANSVERSAL

FIGURE 1. LOCATION MAP OF JACUPIRANGA INDUSTRIAL COMPLEX.

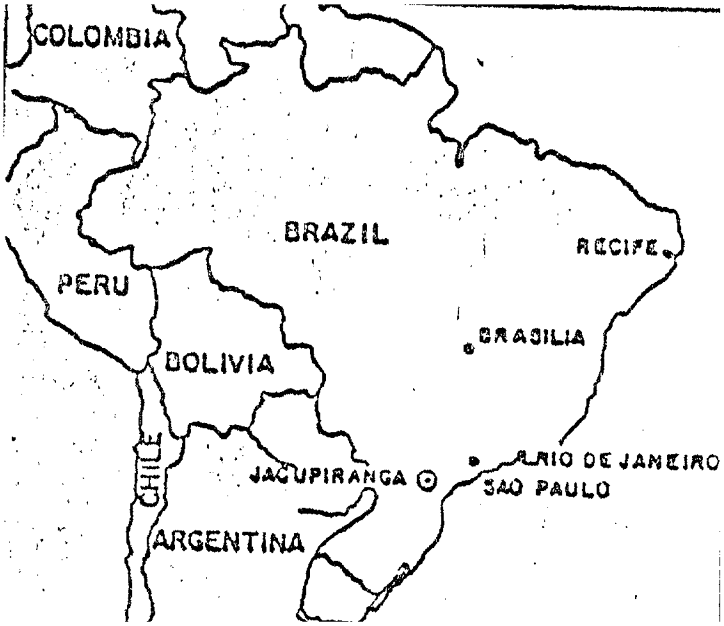


FIGURE 2

SIMPLIFIED FLOW CHART OF THE JACUPIRANGA INDUSTRIAL COMPLEX

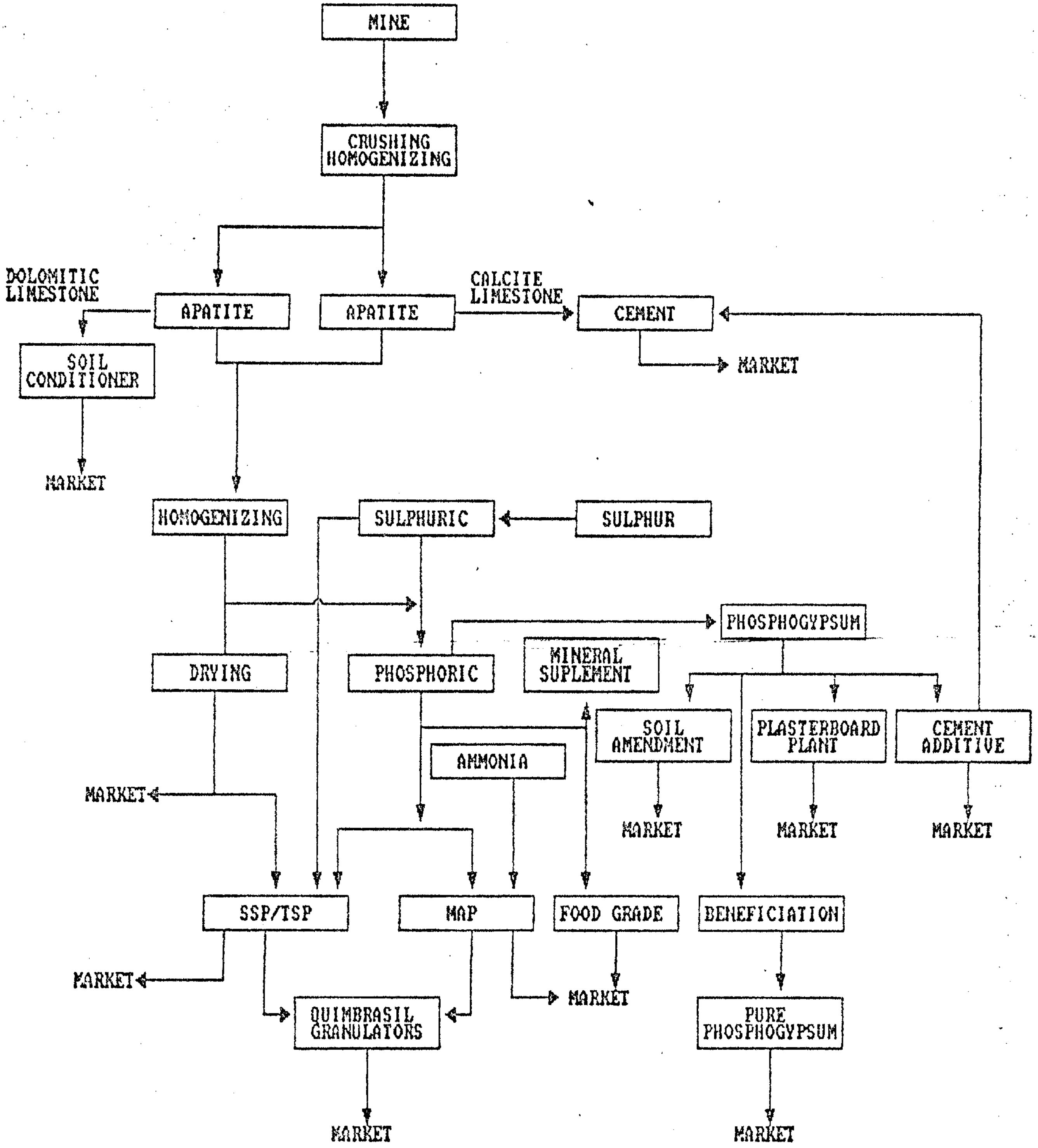
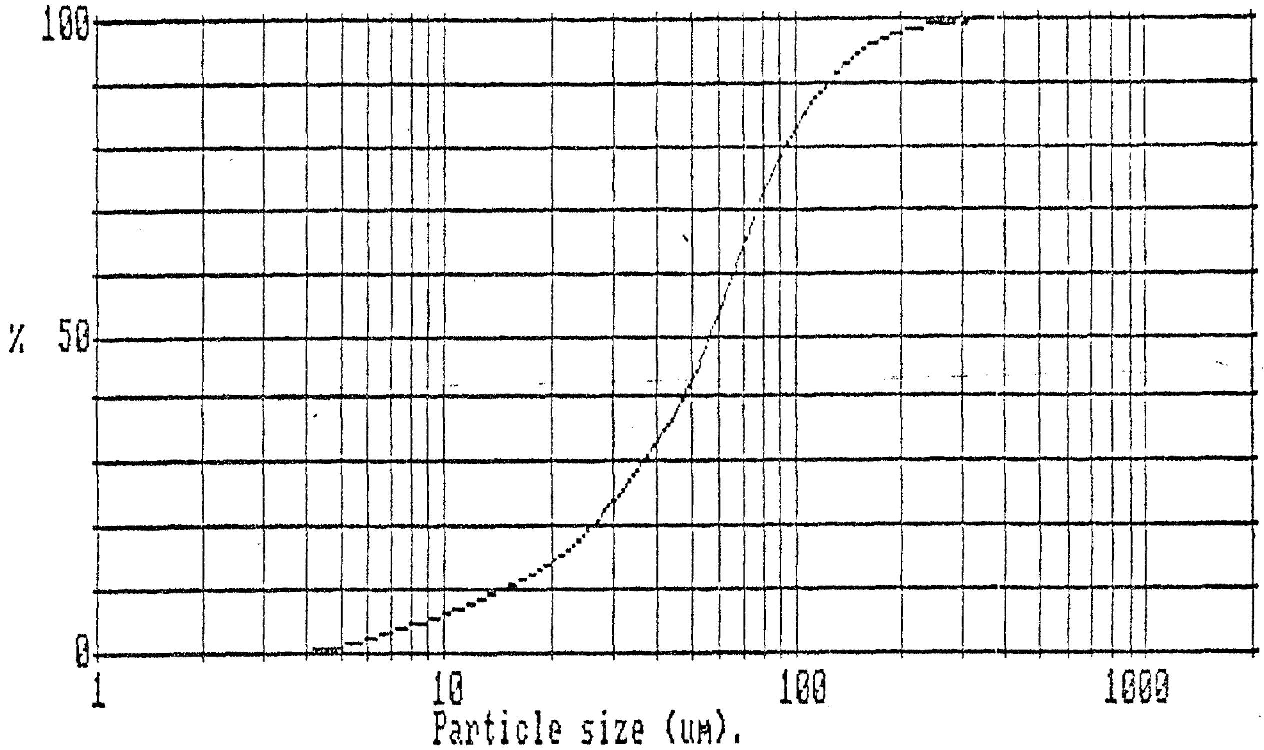


FIGURE 3. RAW PHOSPHOGYPSUM PARTICLES SIZE DISTRIBUTION.

Malvern Instruments MASTER Particle Sizer M3.0 Date 04-12-89 Time 15-08



Sample details:- 1ST. PRODUCT - RAW PHOSPHOGYPSUM

```
Malvern Instruments  MASTER Particle Sizer M3.0 Date 04-12-89 Time 15-08
---------------------------------------------------------------------------------
 Size   |          %     |  Size   |           %     |  Result source=quimb
microns | under  In band| microns | under   in band|  Record No.    = 160
-------------------------------------------------------|  Focal length = 300 mm.
  564.0 | 100.0     0.0 |    53.1 |  45.8      7.5 |  Experiment type pil
  487.0 | 100.0     0.1 |    45.8 |  38.3      5.6 |  Volume  distribution
  420.0 |  99.9     0.1 |    39.5 |  32.7      4.8 |  Beam length  =   2.0 mm.
  362.0 |  99.8     0.2 |    34.1 |  27.9      4.4 |  Obscuration  =0.1946
  312.0 |  99.6     0.3 |    29.4 |  23.5      4.0 |  Volume Conc. = 0.1114 %
  270.0 |  99.3     0.5 |    25.4 |  19.4      3.4 |  Log. Diff.   =3.66
  233.0 |  98.8     0.8 |    21.9 |  16.0      2.6 |  Model indp
  201.0 |  98.0     1.4 |    18.9 |  13.5      2.1 |
  173.0 |  96.6     2.2 |    16.3 |  11.4      1.7 |  D(v,0.5)    =  56.8 m
  149.0 |  94.4     3.1 |    14.1 |   9.6      1.6 |  D(v,0.9)    = 123.1 m
  129.0 |  91.2     4.4 |    12.1 |   8.0      1.4 |  D(v,0.1)    =  14.6 m
  111.0 |  86.9     5.6 |    10.5 |   6.6      1.3 |  D(4,3)      =  65.9 m
   95.9 |  81.3     7.3 |     9.0 |   5.3      1.2 |  D(3,2)      =  32.0 m
   82.7 |  74.0     8.9 |     7.8 |   4.1      1.1 |  Span        = 1.9
   71.4 |  65.2     9.8 |     6.7 |   3.0      1.1 |  Spec. surf. area
   61.6 |  55.3     9.5 |     5.8 |   1.9      0.9 |     0.04 sq.m./cc.
---------------------------------------------------------------------------------
Sample details:- 1ST. PRODUCT - RAW PHOSPHOGYPSUM
```

FIGURE 4. RAW PHOSPHOGYPSUM CRYSTALS SHAPE AND IMPURITIES.

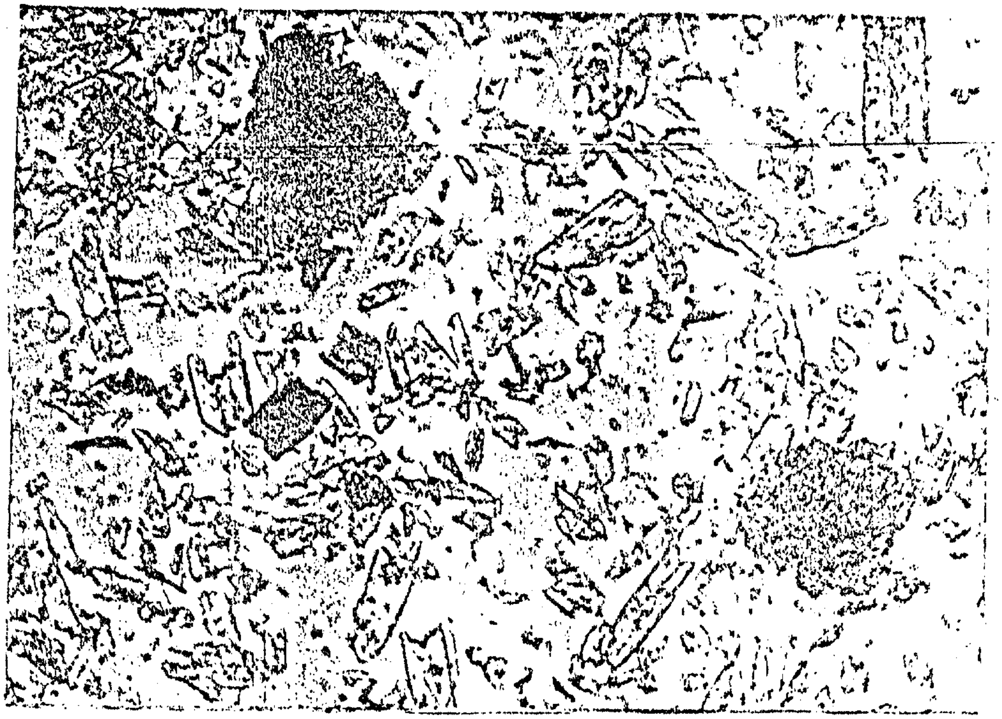


FIGURE 6. PURE PHOSPHOGYPSUM.

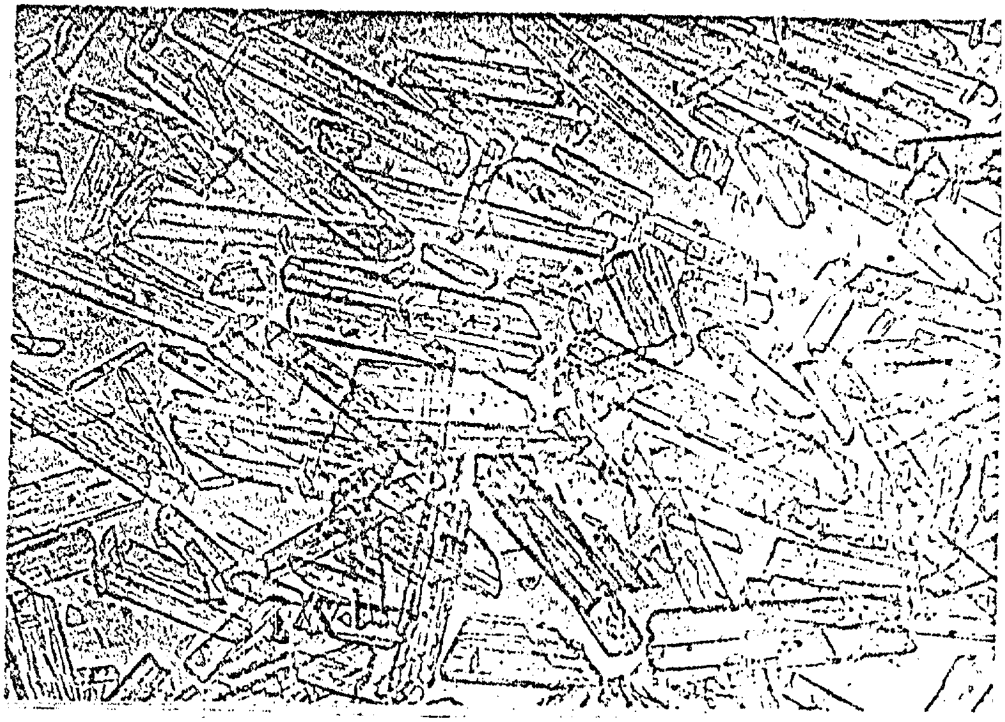


FIGURE 5

LABORATORY PROCESS DEVELOPMENT

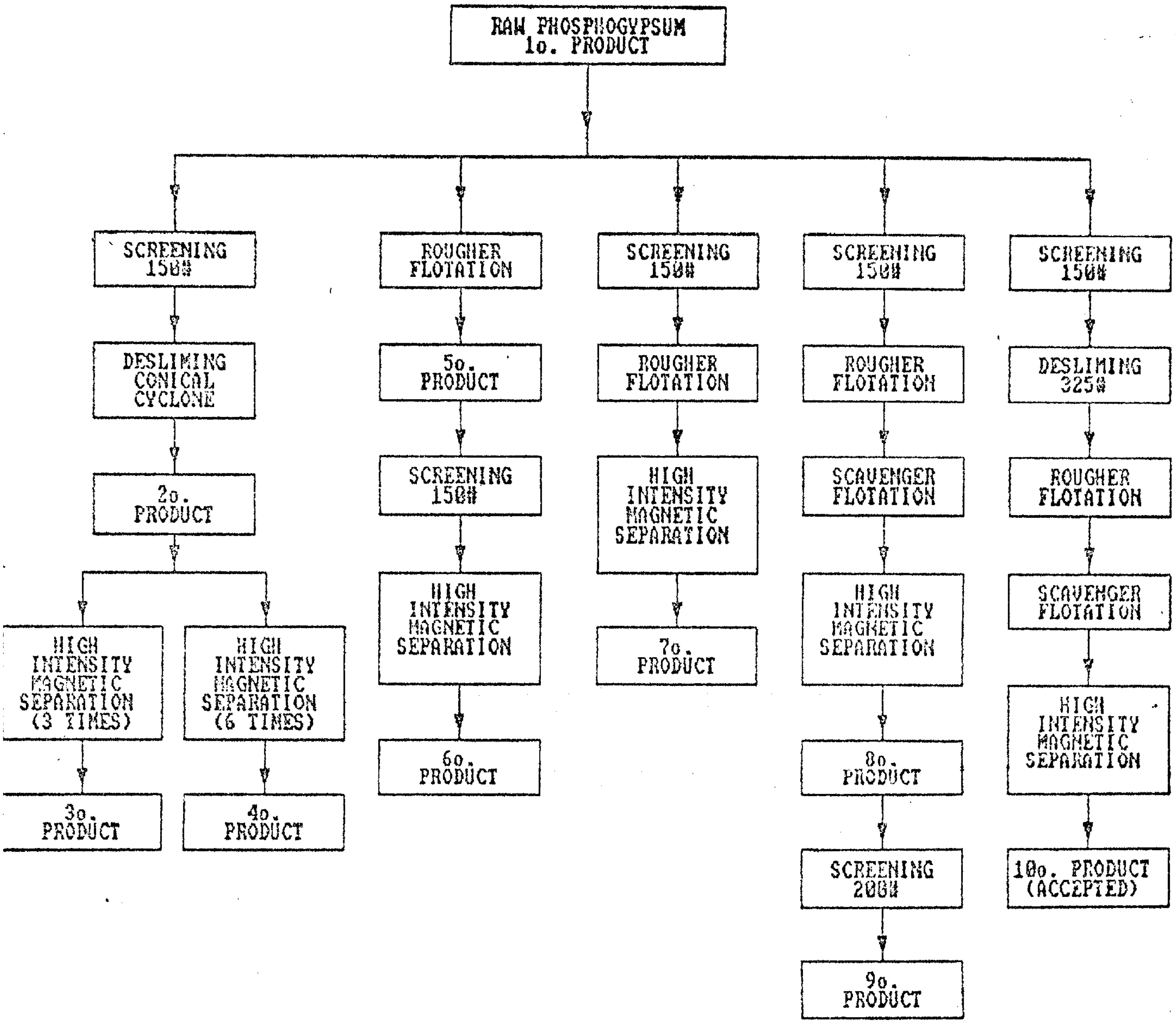
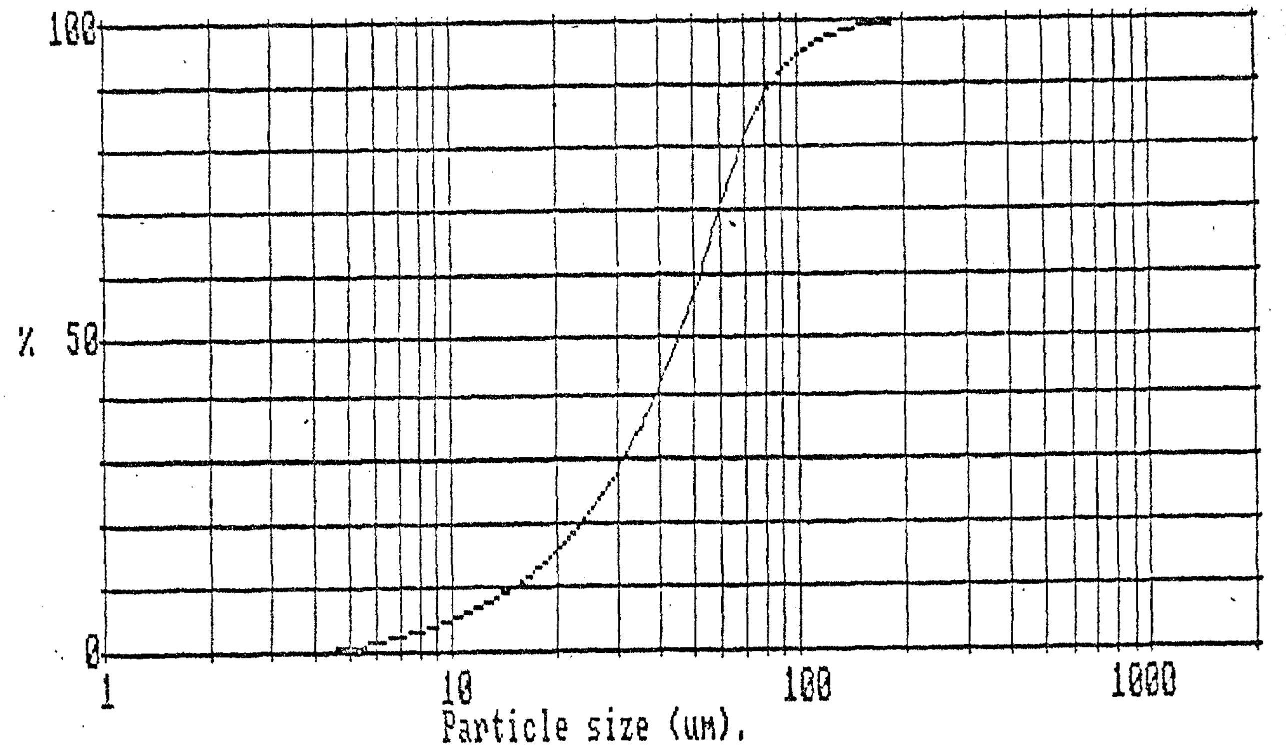


FIGURE 7. PURE PHOSPHOGYPSUM PARTICLES SIZE DISTRIBUTION.

Malvern Instruments MASTER Particle Sizer M3.0 Date 04-12-89 Time 15-15



Sample details:- 10TH. PRODUCT - PURE PHOSPHOGYPSUM

```
Malvern Instruments  MASTER Particle Sizer M3.0 Date 04-12-89 Time 15-15
------------------------------------------------------------------------------
  Size   |            %     |  Size    |              %     |   Result source=quimb
microns  | under  in band | microns  | under   in band |   Record No.    = 161
--------------------------------------------------------|   Focal length = 300 mm.
  564.0  | 100.0      0.0 |    53.1  |  60.9     10.8  |   Experiment type pil
  487.0  | 100.0      0.0 |    45.8  |  50.1      8.9  |   Volume  distribution
  420.0  | 100.0      0.0 |    39.5  |  41.2      7.2  |   Beam length  =   2.0 mm.
  362.0  | 100.0      0.0 |    34.1  |  34.0      6.1  |   Obscuration  =0.1535
  312.0  | 100.0      0.0 |    29.4  |  28.0      5.3  |   Volume Conc. = 0.0804 %
  270.0  |  99.9      0.1 |    25.4  |  22.7      4.5  |   Log. Diff.   =3.71
  233.0  |  99.9      0.1 |    21.9  |  18.2      3.7  |   Model indp
  201.0  |  99.7      0.3 |    18.9  |  14.5      2.9  |
  173.0  |  99.4      0.5 |    16.3  |  11.6      2.3  |   D(v,0.5)     =  45.7 m
  149.0  |  98.9      0.9 |    14.1  |   9.2      2.0  |   D(v,0.9)     =  83.8 m
  129.0  |  98.0      1.5 |    12.1  |   7.2      1.6  |   D(v,0.1)     =  14.8 m
  111.0  |  96.5      2.5 |    10.5  |   5.6      1.4  |   D(4,3)       =  49.6 m
   95.9  |  94.0      4.5 |     9.0  |   4.3      1.1  |   D(3,2)       =  29.7 m
   82.7  |  89.5      7.1 |     7.8  |   3.2      1.0  |   Span         = 1.5
   71.4  |  82.4      9.9 |     6.7  |   2.2      0.8  |   Spec. surf. area
   61.6  |  72.5     11.6 |     5.8  |   1.4      0.7  |       0.06 sq.m./cc.
------------------------------------------------------------------------------
Sample details:-  10TH. PRODUCT - PURE PHOSPHOGYPSUM
```

PILOT PLANT PRODUCTION

FROM JUNE TO OCTOBER '89

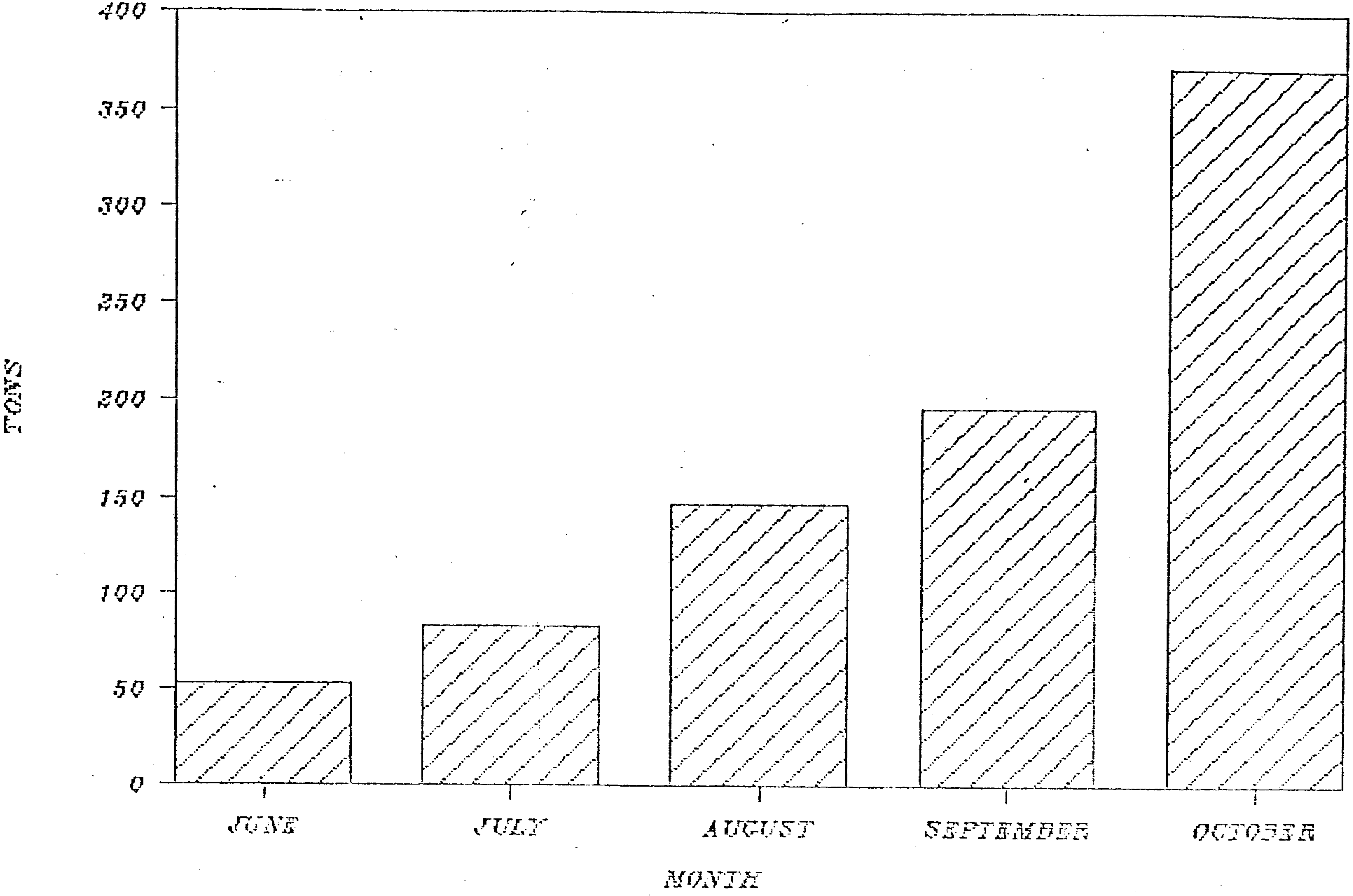
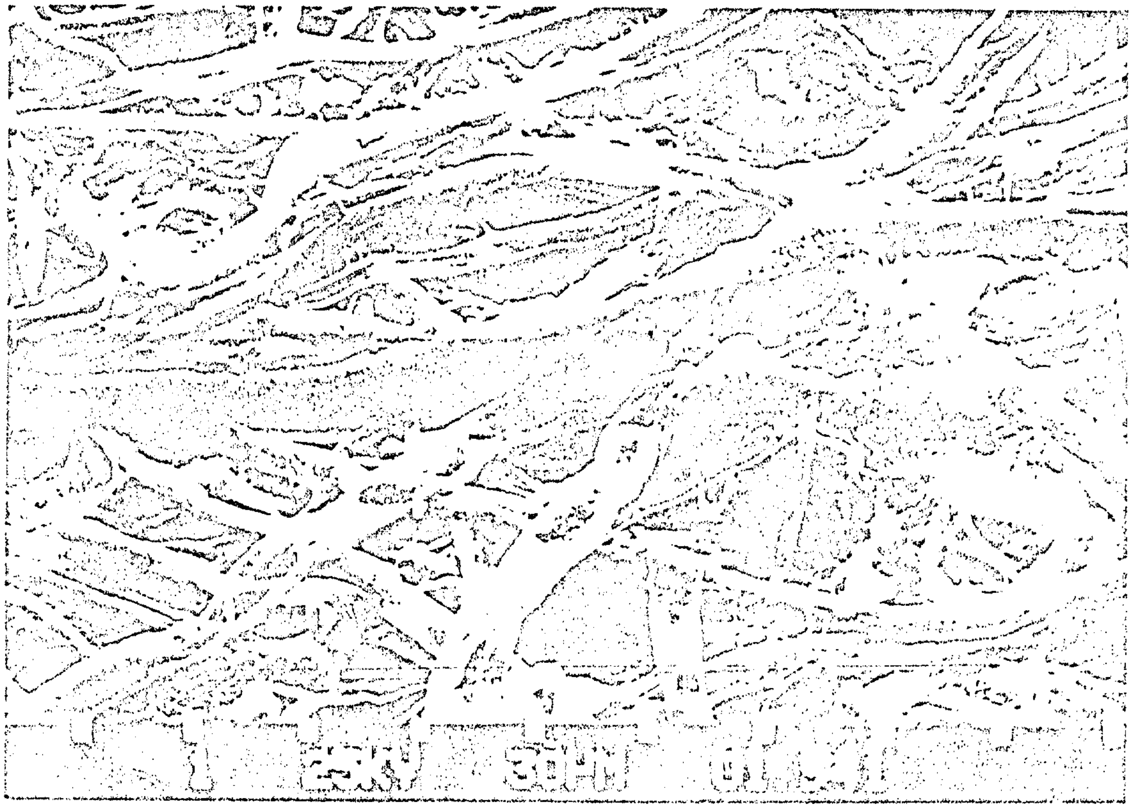
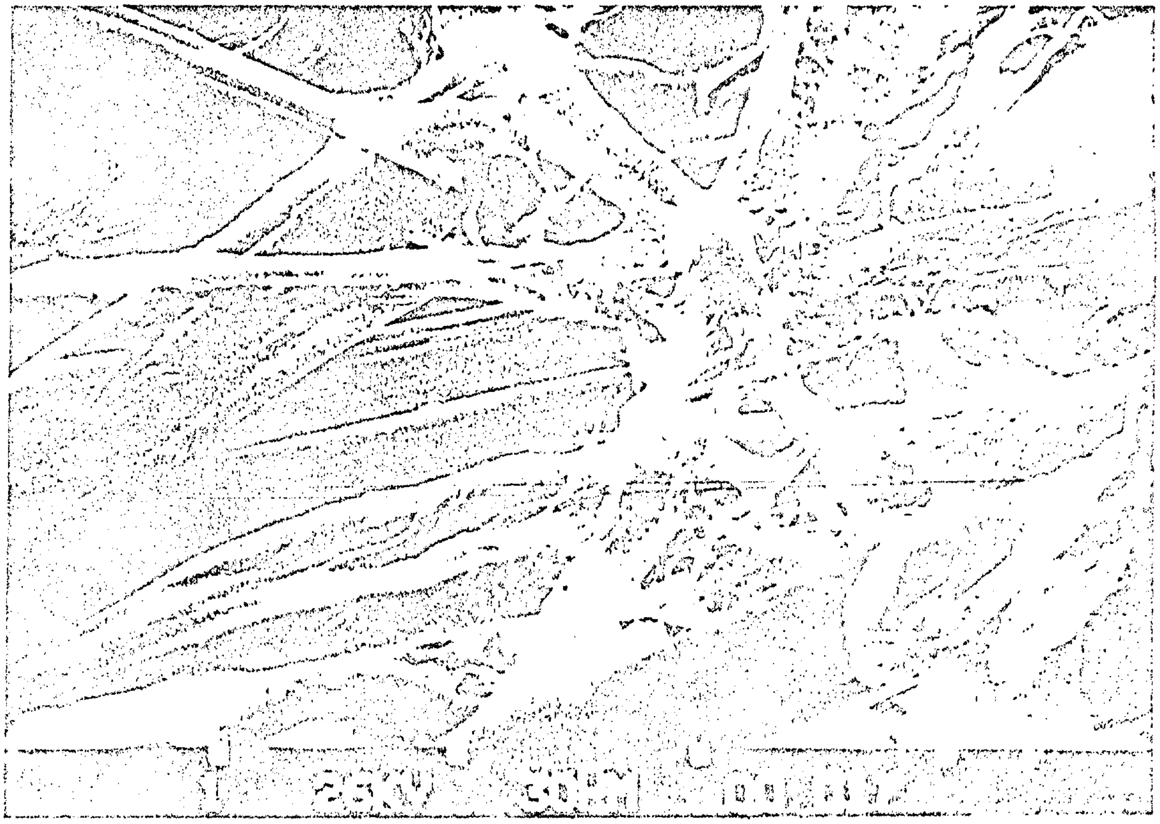


FIGURE 9. COMPARISON BETWEEN PAPER MADE WITH PULP AND PHOSPHOGYPSUM.

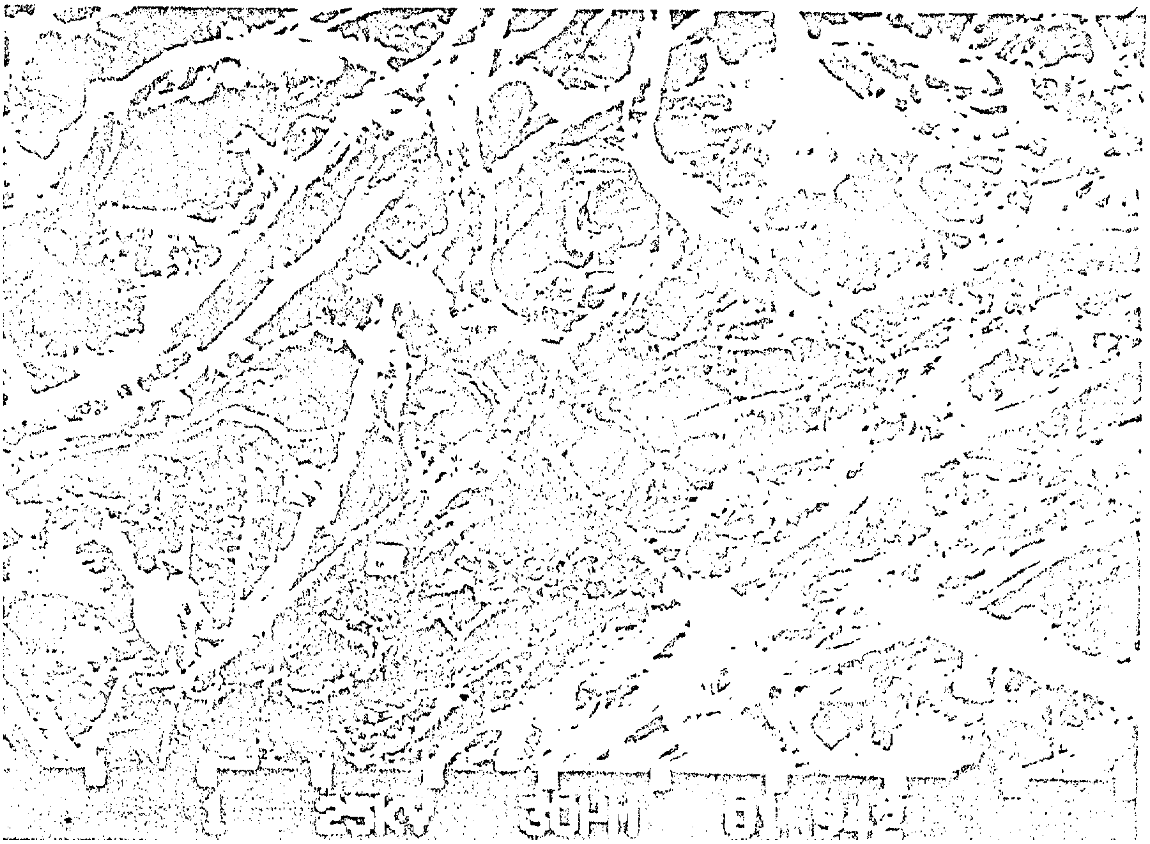


PAPER MADE WITH PULP (100% CELLULOSE) - 500X

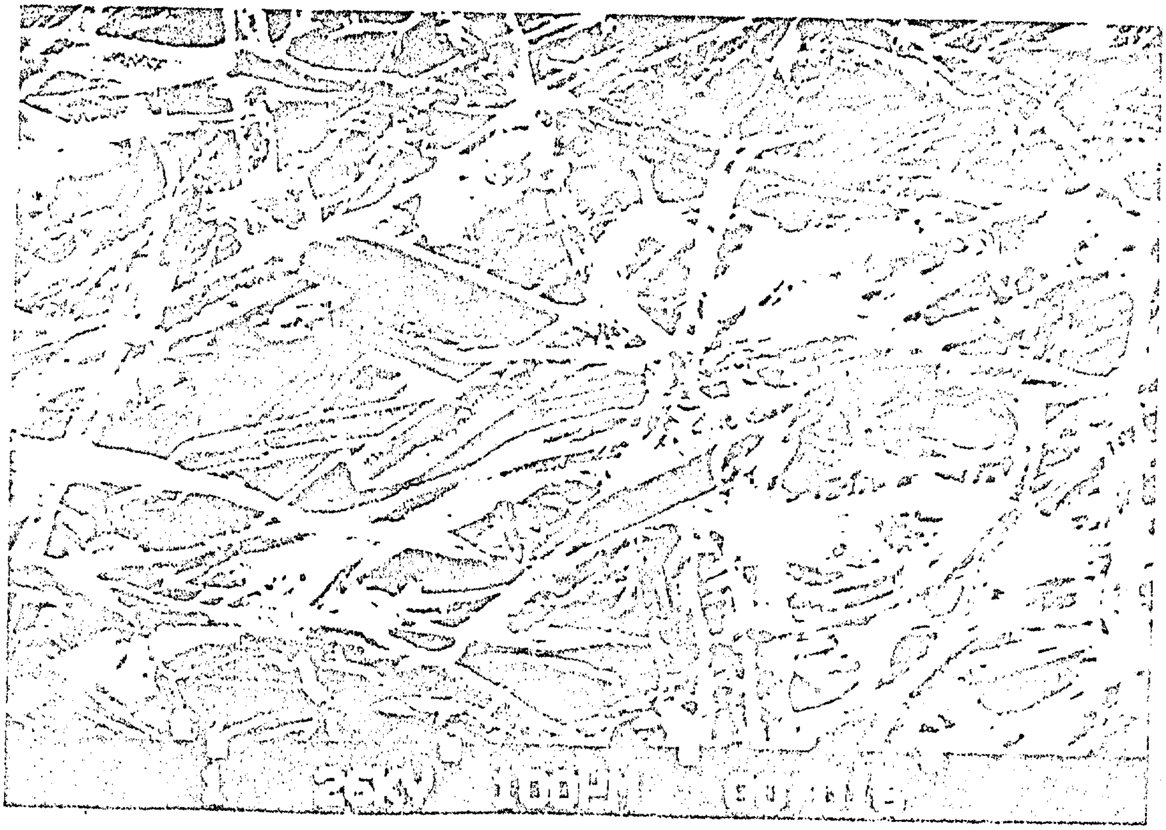


PAPER MADE WITH PURE PHOSPHOGYPSUM (60%) -- 1000X

FIGURE 10. COMPARISON BETWEEN PAPER MADE WITH KAOLIN AND PHOSPHOGYPSUM



PAPER MADE WITH KAOLIN (40%) - 500X



PAPER MADE WITH PURE PHOSPHOGYPSUM (60%) - 300X

THERMAL PROCESSING OF PHOSPHOGYPSUM

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Laboratory of Tallinn Technical University
M.Veiderma, D.Sc., Vice-president of Estonian Academy of
Sciences

A complex of physico-chemical studies and a series of experiments on the reductive decomposition of phosphogypsum (PG) into calcium sulphide or sulphur dioxide and calcium oxide have been carried out by means of laboratory and plant equipment with the fluidized bed reactor. The influence of the composition of raw PG and the reducing gases on the parameters of the process and the quality of the products has been shown. The initial data for the design of the experimental plant for producing CaO and SO_2 have been presented.

INTRODUCTION

From the variety of processes of utilizing PG we have been studying the process of its thermochemical decomposition in order to obtain CaS or SO_2 and CaO (Figure 1). The above process is of grate importance for the factories producing mineral fertilizers as it enables to regenerate an essential part of the sulphuric acid used up in the production of wetprocess phosphoric acid from natural phosphates within the same plant. The difference in our approach lies in the use of a fluid bed reactor in addition to the common stationary one and in the reduction of phosphogypsum by gaseous reductants (CO and H_2) obtained from an incomplete burning of natural gas, as well as in the determination of the influence of the composition of raw PG on the parameters of the process and the quality of the products.

LABORATORY EXPERIMENTAL

MATERIALS

Calcium sulphate samples included chemically pure $CaSO_4$, natural gypsum and phosphogypsum from the processing of various natural phosphates by dehydrate regime (Table 1).

METHODS

Thermal analyses of the samples were performed by simultaneous recording of the TG, DTG, and DTA curves on the thermoanalyser Mettler TA-1, SETARAM and OD-103 (MOM, Hungary). The heating rate was 10 or 25 deg/min. Samples (40-70mg) were placed in a standard platinum crucible (diam.

6mm, depth 5mm); in DTA measurement Al_2O_3 was used as a reference material. Measurements were carried out in a dynamic atmosphere of CO or H_2 with a flow rate of 100 ml/min. Carbon monoxide contained 99% CO, 0.3% H_2 and 0.7% $N_2 + O_2$. Pure nitrogen was used as inert component in the gas mixtures.

The kinetics of the decomposition of granulated PG was examined in fluid bed kilns with the cross-sectional area of 30 and 100 cm^2 by burning natural gas with an air expenditure coefficient (a) in the range of 0.50-0.95.

Table 1. Origin and characteristics of the calcium sulphate samples. Contents calculated on dry material bases.

Sample	$CaSO_4$ %	Impurities % Total	SiO_2
1.Reactive $CaSO_4$ (chem. pure)	99.86	0.14	-
2.Natural gypsum	95.08	4.92	0.20
3.Phosphogypsum from Kola apatite concentrate	94.89	5.11	0.37
4.Phosphogypsum from Tunesian phosphorite	90.47	9.53	1.0
5.Phosphogypsum from Karatau phosphorite	80.75	19.25	14.75
6.Phosphogypsum from Toolse phosphorite	83.74	16.26	14.18
7.Phosphogypsum from Karatau phosphorite	75.80	24.20	11.99

To obtain Ca) and SO_2 natural gas was burned straightly in the zone of granulated particles, while CaS was obtained in a separate compartment.

The composition of the solid residue was determined by means of a powder difractometer (DRON-l, Philips PW 1050) and an IR-spectrometer (SPECORD 75IR, PERKIN ELMER 521); that of the gaseous phase by a gas chromatograph (LHM-8MD, Beckman GC-2) employing a Porapack Q-filled column.

RESULTS AND DISCUSSION

Decomposition of $CaSO_4$ in CO and H_2

The above mentioned gaseous reductants react with $CaS0_4$ - the main component of PG - according to the following summary equations (Wheelock, Boylan, 1960, Vladimirov, Gavrilova, 1978, Kostylkov, Nosov, 1982, etc.):

$$CaSO_4 + 4CO \text{ -- } CaS + 4CO_2 + \Delta H \qquad (1)$$

$$CaSO_4 + CO \text{ -- } CaO + SO_2 + CO_2 - \Delta H \qquad (2)$$

By means of thermogravimetric analyses it was established that decomposition of $CaSO_4$ in a carbon monoxide medium according to reaction equation (1) occurs at a temperature of 740-750 °C and above , reaching its maximum rate at the range of 950-1000 °C (Figure 2).

A drop in the rate of reaction (1) as well as a decrease in the degree of conversion of $CaSO_4$ into CaS is caused by reaction (2) which starts at 950 °C and is considerably enhanced by the rise of temperature. The course and relative rates of these reactions are essentially affected also by the content of the reductants in the gaseous phase. For example, if the concentration of reductants (CO) in the gaseous phase decreases to 5% (Vol.), reaction (2) starts at 800-810 °C and the yield of CaS diminishes respectively. At this content of CO the rates of reactions (1) and (2) become equal at 1030 °C. At temperatures above 1170-1180 °C only reaction (2) takes place and the solid product is mainly calcium oxide. Similar results have been obtained also by H_2. On the basis of calculated values of the apparent activation energy and the rate constants of these reactions, it has been stated that the process is limited mainly by the chemical reaction (Kuusik, Trikkel, 1985).

Influence of impurities

Depending on the kind of phosphate rock and the conditions of extraction of phosphoric acid there can be a noticeable content of mineral impurities (SiO_2, fluorine, ferric and aluminium compounds, uncomposed apatite etc.) in PG. It has been determined that these impurities do not change only the composition of the final solid products but also the conditions of the process of reduction of $CaSO_4$ (Kuusik,et a1.,1985). With an increase in the content of impurities (samples 2-6) the decomposition temperatures. become 70 to 100 degrees lower (Figure 3).

Reducing PG by the products of incomplete combustion of natural gas, the reducing gases contain, besides H_2 and CO, also up to 20% of water vapour and 10% of carbon dioxide.

It has been established experimentally that both H_2O vapour and CO_2 decrease the yield of CaS obtained by reaction (1), however the effect of carbon dioxide is larger, The greatest slow down in the reaction rate is noticed when both the impurities are present (Trikkel, Kuusik, 1986). The undesirable influence of H_2O and CO_2 can be compensated by raising the temperature, but the rate of reaction (2) increases at the same time.

Thermodynamics

The above-mentioned experimental data agree with the results of thermodynamic calculations which allow us to assess the possibility and direction of the reactions while changing the conditions of the process, namely the composition of the gaseous phase and the content of SiO_2 and Fe_2O_3 in PG (Figure 4). It can be concluded that in order to increase the field of existence of CaS relatively low temperature and high reducing potential of the reducing gases are needed (Trikkel,et al.,1989). It would also be good to add small amounts of solid reductant to the initial PG to make reaction (1) run more completely by promoting the increase of the reducing potential of the medium as a result of binding up oxygen or CO_2. At the same time more carbon monoxide is liberated.

The presence of mineral impurities such as ferric and aluminium oxides and silica leads to the decrease of the field of $CaSO_4$ (Fig.4 B), and most likely also of the field of existence of CaS. Consequently, it would be better to obtain calcium sulphide on the basis of pure PG, obtained from apatite concentrate (sample 3, Table 1), for example. However, the process of getting lime by reaction (2) can be run to a certain extent even better on the basis of PG which contains more impurities in case the purity of the final product is not important.

Experiments in fluid bed furnace

The conditions for selective processing of CaS or SO_2 and CaO, determined by physico-chemical studies, were experimentally specified in the fluidized bed furnace. The required conditions were established to be for getting CaS the temperature between 880-900° C and the content of reductants (H_2 + CO) in the gaseous phase at about 15-25%. Such conditions are obtained by burning natural gas at α= 0.50-0.55. In these conditions the 75% degree of reduction of $CaSO_4$ is achieved in 30-35 minutes (Figure 5 A). With the help of modifying additives, especially semicoke which has a high content of volatile components and is the most effective one, the same degree of reduction can be achieved in 10-12 min. The solid product contained 66-70% CaS, 10-14% CaO and 1-2% $CaSO_4$. It can be used as a semiproduct for subsequent processing of sulphur or sulphuric acid (by the Claus process) or as an independent final product - a sulfidiser in non-ferrous metallurgy. However, the presence of SO_2 in the exhaust gases makes purification indispensable.

The appropriate conditions for getting SO_2 and CaO were established to be the temperature 1130-1200 °C and concentration of reductants 5-15%. In this case the degree of conversion of PG equal to 90% and even more can be achieved in 5-7 minutes (Kuusik,et al.,1981).

Mineral impurities in PG enhance the decomposition process but diminish considerably the CaO content in the final product (Figure 5 B).

PILOT PLANT EXPERIMENTS

On the basis of the data obtained on the process of decomposition of PG into CaO and SO_2 a technological scheme has been worked out and the process has been tested on plant equipment using a two-zone fluidized bed kiln with the diameter of 1 m (Figure 6). Experimental work was carried out in co-operation with the Research Institute of Fertilizers and Insecto-Fungicides (Moscow, U.S.S.R.) and the Institute of Chemistry and Technology (Sofia, Bulgaria) where PG with the composition corresponding to that of probes number 3 and 4 was used.

Optimum conditions for the process have been established as follows: temperature in the reaction zone between 1150-1180 °C, a = 0.80-0.85, specific load rate 1.2-1.3 t/sq.m hr. The sulphur dioxide content in the flue gases from one-zone furnace stayed between 6-8%, from the two-zone furnace rose up to 9-10% (Solodjankina,et a1.,1981, Borissov,et al., 1982). Utilizing the heat of flue gases for heating the raw material and air for burning the relative economy of fuel appeared to be about 40-45% and an SO_2 concentration of about 12-13% (Vol.) was achieved (Tint, Kuusk,1983).

It must be noted that Dr.V.A.Yershof has recommended a process of decomposing PG in an electric furnace, with the addition of pyrites that allows gases containing up to 60% and more of sulphur dioxide to be obtained (Kuzhnetsova, et al., 1985).

The quality of phospholime depends on the composition of raw PG (Figure 7). As a result of combining a part of CaO into silicates the content of active CaO in phospholime obtained from phosphorite phosphogypsum is lower than calculated (Kuusik, Taremaa,l988). Phospholime obtained from phosphorite phosphogypsum can be successively used in the processing of autoclave concretes (Kuusik,et al.,1984). Phospholime obtained from apatite phosphogypsum with the Ca0 content of about 75-80%, can be used in different branches of industry, as a means for neutralizing mineral fertilizers (Kuusik,et al., 1985) and exhaust water, as well as for desulphurization of flue gases.

CONCLUSION

A scientific and technical basis for the process for thermal utilization of PG to produce CaS or SO_2 and CaO has been worked out. Technological schemes and the regulations of these processes have been drawn, the apparatus has been recommended and initial data for the design of an experimental plant have been presented. The carrying out of these processes allows to regenerate about 80% of the sulphuric acid used up in the production of wetprocess H_3PO_4, to decrease the operation expenses and improve the surroundings in the processing region.

ACKNOWLEDGEMENTS

The authors wish to thank A.Trikkel and A.Kuusk for participating in our work.

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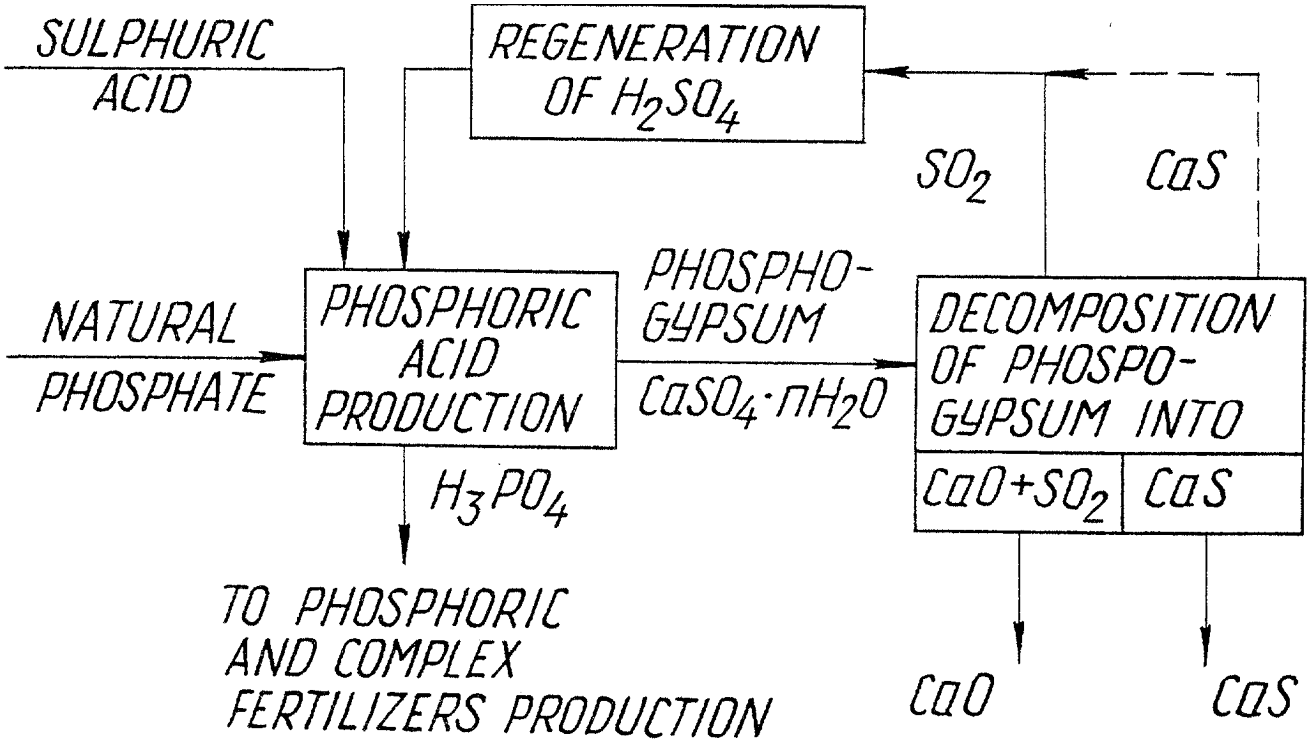

FIG.1. Flow diagram of waste-free production of phosphoric and complex fertilizers.

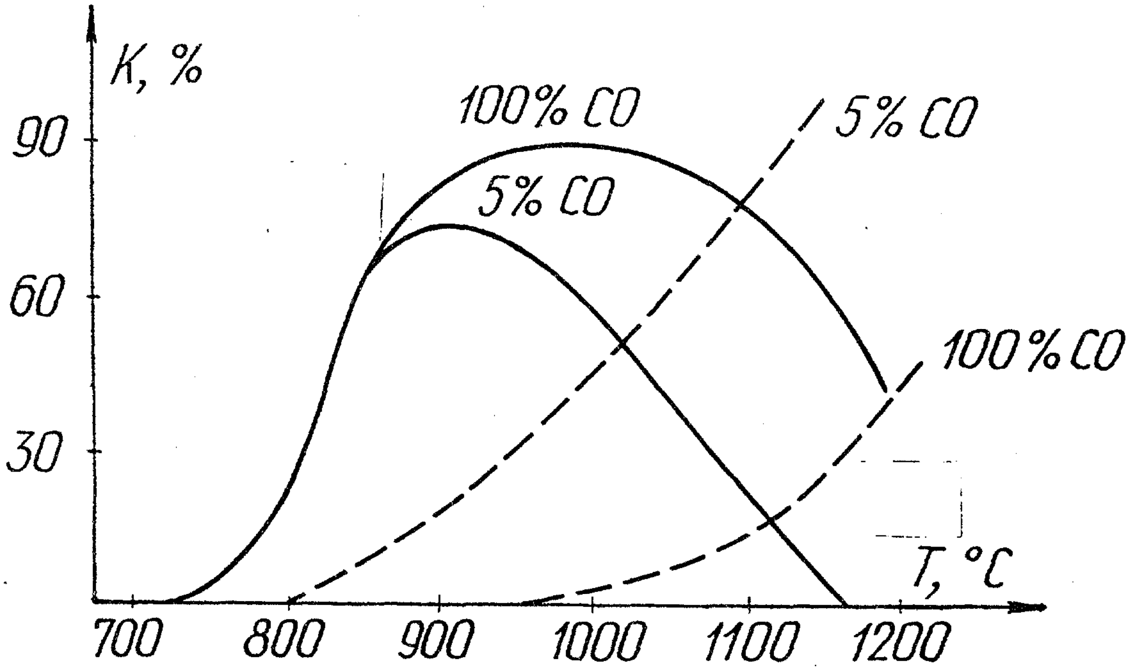

FIG.2. The influence of the process temperature (T, °C) and CO concentration on the degree of conversion (K,%) of pure $CaSO_4$ at constant duration of heating. (——) reaction (l), (-----) reaction (2).

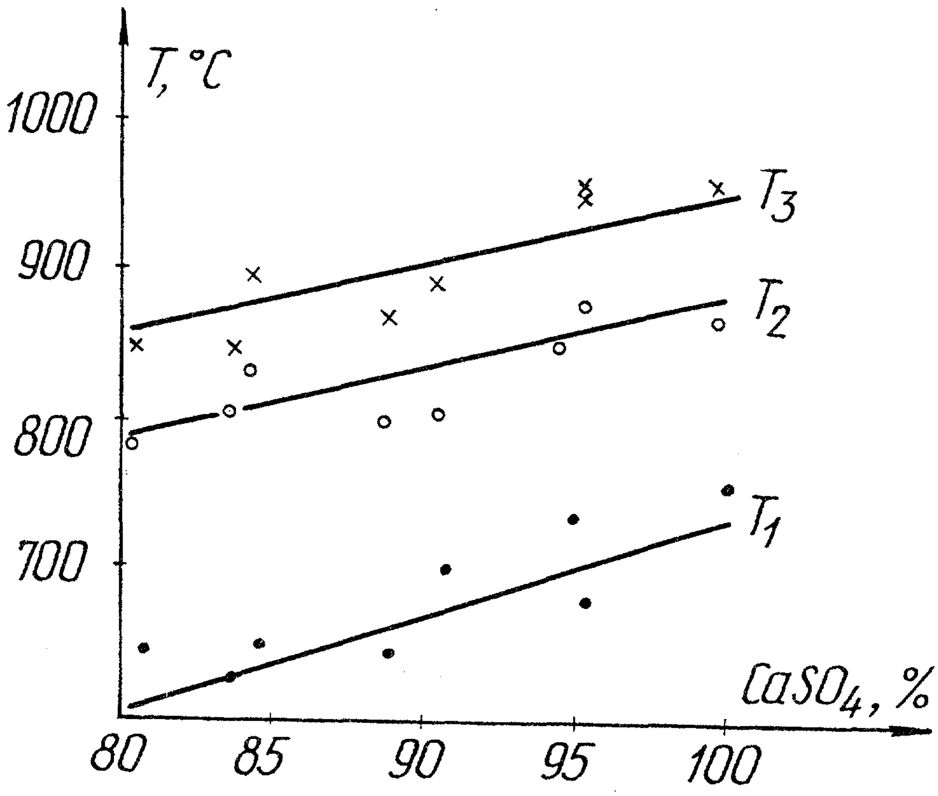

FIG.3. The variation of decomposition temperatures as a function of the $CaSO_4$ content of the samples. T_1, T_2 and T_3 are the thermogravimetric starting, maximum rate and end temperatures.

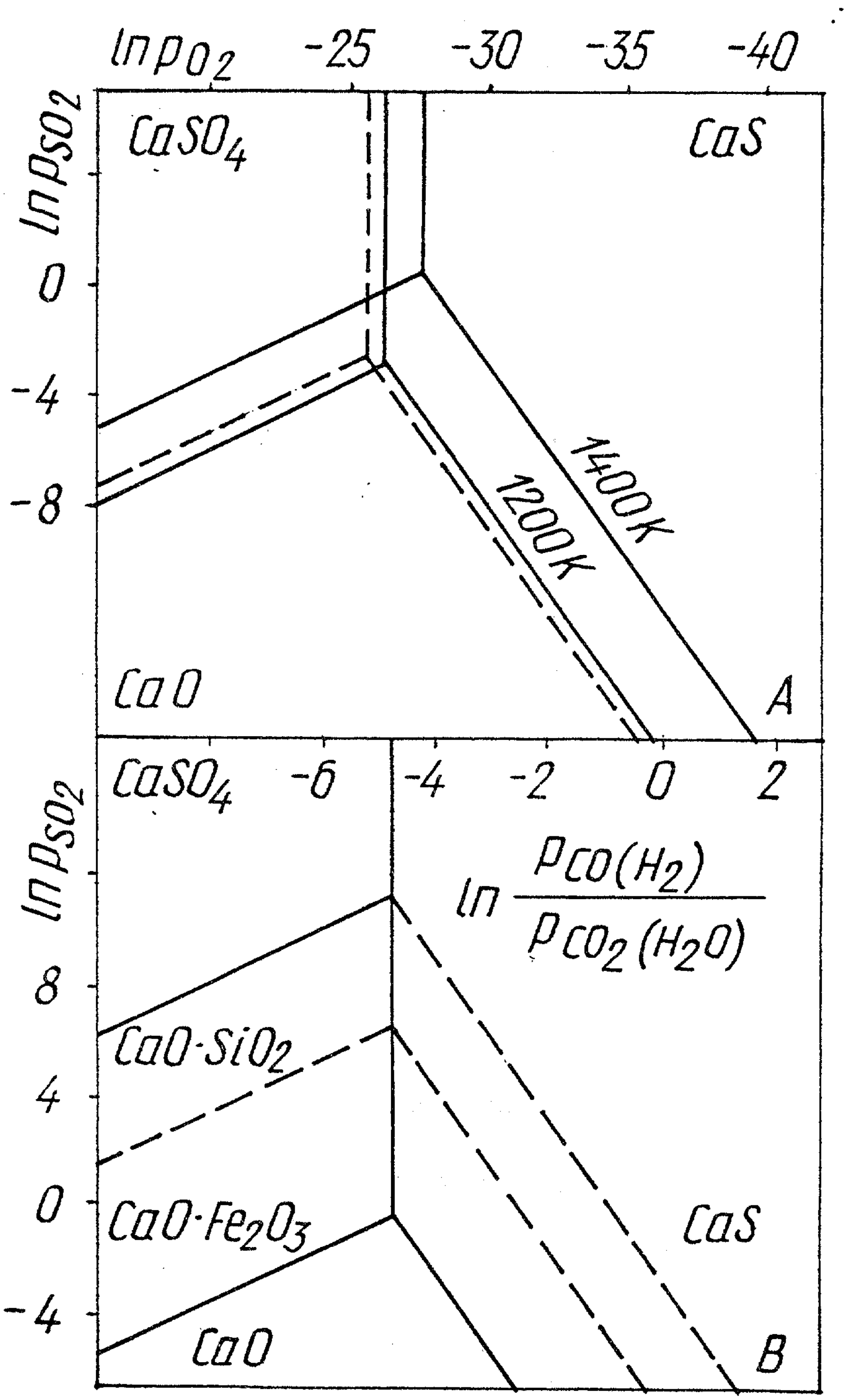

FIG.4. State diagrams of the $CaSO_4$ - CO - CO_2 (——) and $CaSO_4$ - H_2 - H_2O (- - -) systems as functions of the reducing potential and partial pressure of SO_2 (A) and of the influence of impurities in PG (B).

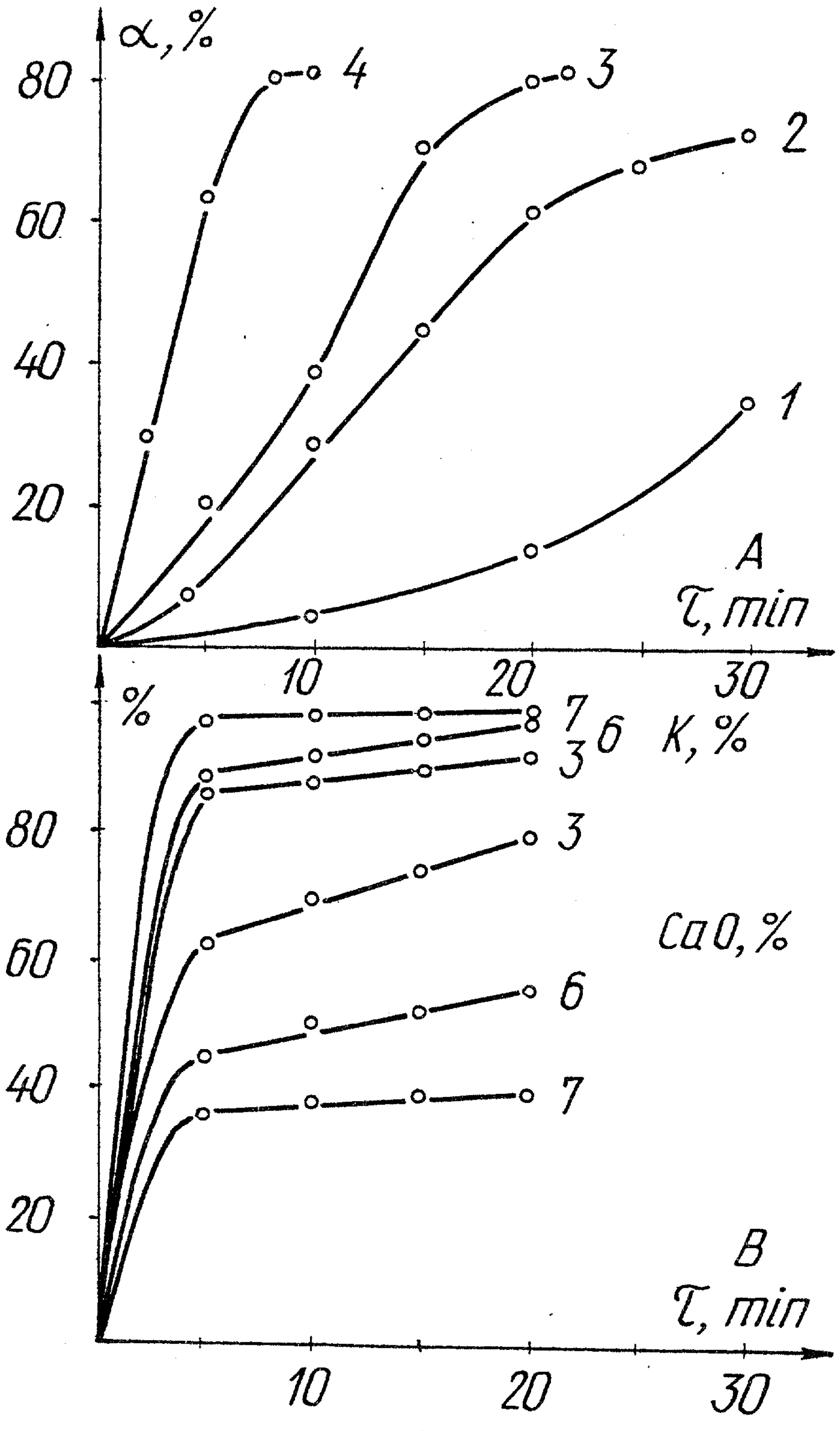

FIG.5. Kinetic curves of PG decomposition:

A) The influence of the process conditions on the degree of $CaSO_4$ conversion into CaS (α, %). 1-stationary bed, 2-fluid bed, 3,4-fluid bed, with additives.

B) The influence of the composition of raw PG on the degree of $CaSO_4$ conversion into CaO (K,%) and on the content of active CaO (CaO,%) in the product. The numbers refer to the samples listed in Table 1.

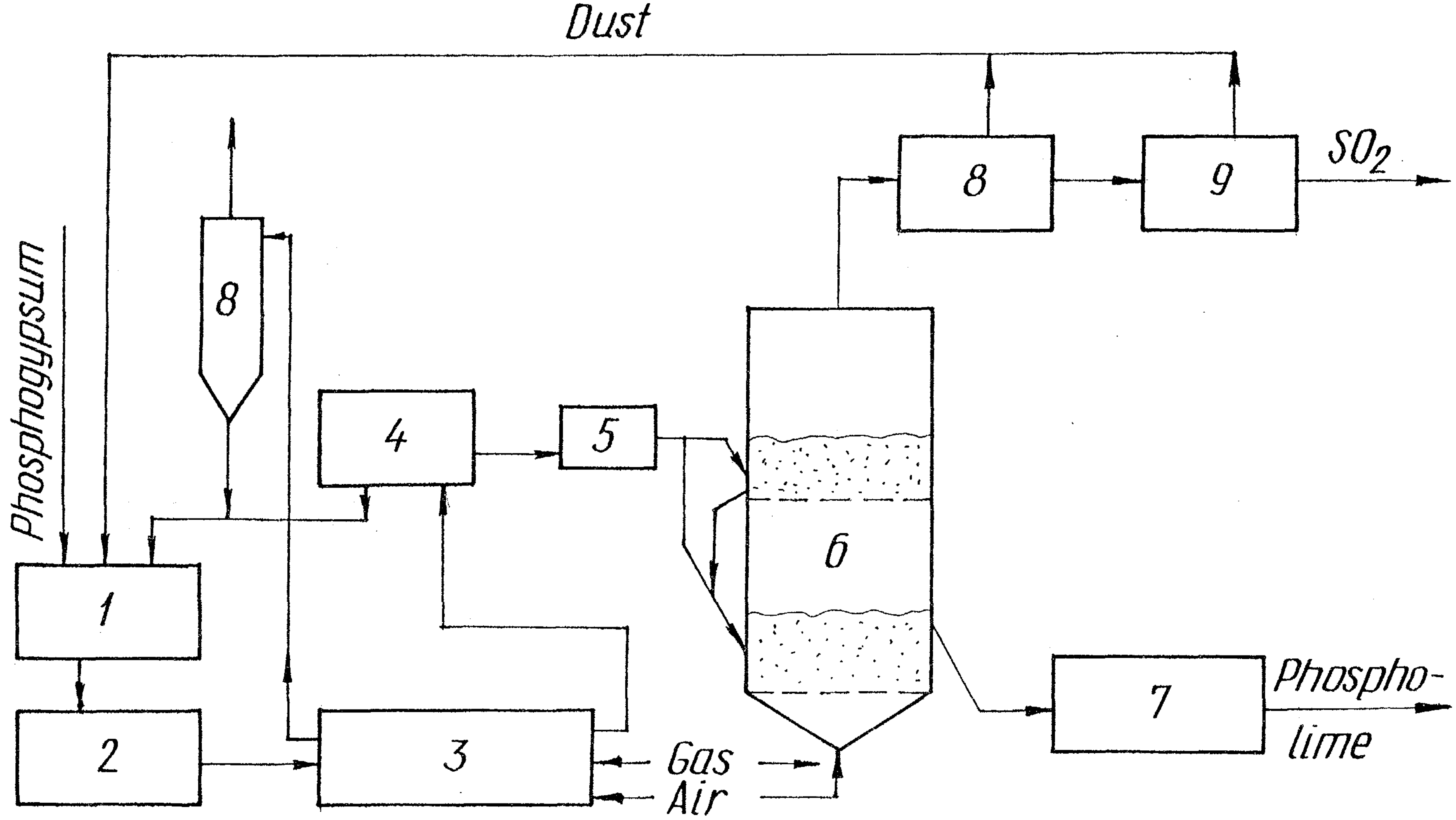

FIG.6. Technological scheme of the pilot plant equipment. l-mixing, 2-granulation, 3-drying, 4-classification, 5-feeder, 6-fluid-bed furnace, 7-cooling, 8,9-gas purification (cyclone, electrofilter).

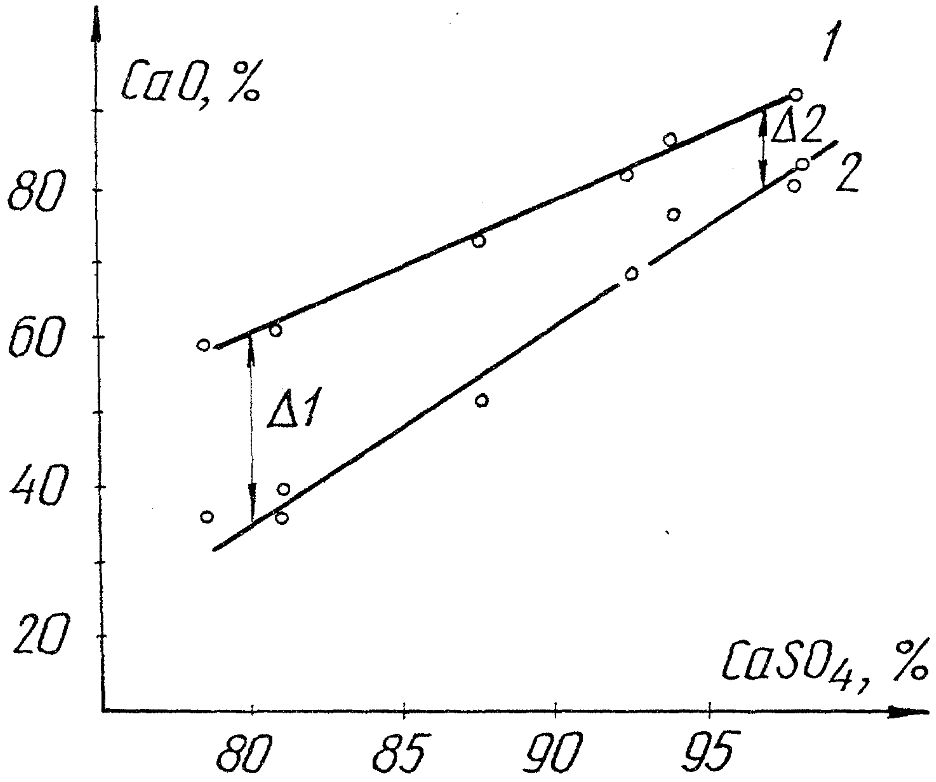

FIG.7. Calculated (1) and actual (2) content of active CaO (CaO,%) as a function of $CaSO_4$ content ($CaSO_4$, %) in raw PG.

DECOMPOSITION OF GYPSUM IN A TWO-STAGE FLUIDIZED BED REACTOR

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ABSTRACT

A two-stage fluidized bed process was demonstrated for decomposing waste gypsum into sulfur dioxide and quicklime. A bench-scale reaction system was employed in which one fluidized bed stage was placed directly above another. Feed particles were preheated in the upper stage by direct contact with the hot gas rising from the second stage. After preheating, the particles descended to the lower stage where they reacted with a mixture of gases produced by partial combustion of natural gas; The natural gas flow was cycled on and off to produce conditions which were alternately reducing and oxidizing. The reacted particles were removed from the lower stage through an overflow tube.

Operation of the bench-scale system demonstrated several important advantages for the two-stage process. By recovering heat from the off-gas to preheat the feed, fuel and air requirements were reduced in comparison to the requirements of a single-stage process. Also decrepitation of feed particles was reduced since the particles experienced less thermal shock in the two-stage process. Due to the lower gas velocity and reduced decrepitation, the elutriation of fines from the reactor was reduced and

the yield of quicklime was improved. In addition, the concentration of sulfur dioxide was enhanced.

INTRODUCTION

Recent improvements in a process for converting waste gypsum into sulfur dioxide and quicklime could benefit the phosphate industry by providing an economical method for utilizing phosphogypsum as a raw material for the production of sulfuric acid. Although a promising method for decomposing calcium sulfate has been under development at Iowa State University for sometime, there has been a need to improve the operating efficiency and economics of the process. This need will be satisfied at least in part by the improvements which are described, below.

The basic method for decomposing calcium sulfate contained in phosphogypsum and other materials was demonstrated previously in bench-scale and larger equipment (Swift and Wheelock, 1975; Wheelock, 1978; Smith et al., 1984; Wheelock and Morris, 1986; Wheelock et al., 1988; Morris et al., 1987). The method employs a two-zone fluidized bed reactor operating at high temperature to decompose calcium sulfate particles. One of the zones is a reducing zone created by burning natural gas or other fuel with a substoichiometric amount of air in the lower part of the fluidized bed, whereas the other zone is an oxidizing zone created by introducing excess secondary air above the reducing zone. Partial combustion of the fuel in the reducing zone produces carbon monoxide and hydrogen which react with calcium sulfate as follows:

$$CaSO_4 + CO \text{ (or } H_2) = CaO + CO_2 \text{ (or } H_2O) + SO_2 \qquad (1)$$

$$CaSO_4 + 4\ CO \text{ (or } H_2) = CaS + 4\ CO_2 \text{ (or } H_2O) \qquad (2)$$

Although reaction (1) predominates in the reducing zone, some undesirable calcium sulfide is likely to be produced by reaction (2). However, the calcium sulfide is eliminated as the solid particles circulate and pass through the oxidizing zone where the following reactions occur:

$$CaS + 3/2\ O_2 = CaO + SO_2 \tag{3}$$

$$CaS + 2\ O_2 = CaSO_4 \tag{4}$$

Reaction (3) produces the desired products, and while reaction (4) converts calcium sulfide back to calcium sulfate, it is not a problem because the calcium sulfate will have another opportunity to react when the material returns to the reducing zone. After several passes through both reaction zones, the particles are converted almost completely to calcium oxide and are essentially free of calcium sulfide.

While this method has been demonstrated in fluidized bed reactors. ranging up to 25 cm in diameter, the uniform distribution of secondary air in the middle of a large diameter fluidized bed is likely to be difficult and costly. Part of the difficulty is due to the corrosive nature of sulfur dioxide at high temperature which requires the use of ceramic or refractory materials for reactor internals. To circumvent this problem, an alternative method was demonstrated recently for treating calcium sulfate particles to conditions which are alternately reducing and oxidizing (Wheelock and Riel, 1990). The new method involves varying conditions throughout a fluidized bed of reacting particles in a periodic or cyclic manner. This is accomplished by introducing all of the air and fuel through the gas distributor in the bottom of the reactor and varying the air-to-fuel ratio. This completely eliminates the need for secondary air.

For demonstrating the new mode of operation, particles of waste gypsum were treated continuously in a bench-scale fluidized bed reactor which was supplied with natural gas and air (Wheelock and Riel, 1990). While air was supplied at a constant rate, the flow of natural-gas was cycled on and off. In general, the results achieved with the cyclic mode of operation were comparable to those achieved with the two-zone mode of operation with the same reactor.

Another advancement which improves the operating efficiency of the process is the subject of this report. It had been observed previously (Morris et al., 1987) that extensive particle decrepitation took place, probably due to thermal shock, when particles of feed entered a hot fluidized bed. Since the resulting fines were elutriated rapidly from the bed before being reacted completely, the operating efficiency 'was reduced. The apparent solution was to preheat the particles more gradually. To show that this was a practical solution for the problem, a series of runs was conducted with a two-stage fluidized bed system in which the feed was preheated in the first stage by contact with the hot off-gas from the second stage. Consequently, the feed was subjected initially to a lower temperature than it would have been in a single-stage system. The results obtained with the two-stage system are compared below with those obtained with a single-stage system.

REACTION SYSTEM

Particles of calcium sulfate were treated in the two-stage fluidized bed reaction system shown in Figure 1. The main body of the reactor was a silicon carbide tube having an inside diameter of 15.2 cm, wall thickness of 1.3 cm, and height of 1.52 m. The bottom of the tube was fitted with a ceramic gas distributor which had four cone-shaped openings for the admission of air and natural gas. The distributor also accommodated a mullite thermowell and mullite overflow pipe. The top of the reactor body was fitted with a stainless steel cap which was 56 cm high and which flared outward to a diameter of 30.5 cm. The cap was fitted with a feed inlet, off-gas outlet, mullite thermowell, and stainless steel gas sampling tube. A stainless steel can was suspended from a flange placed between the cap and the reactor body. This can served as a container for the upper fluidized bed or feed preheating stage. The can had a diameter of 14 cm and height of 16.5 cm. The bottom of the can had 25 holes which were 1.11 cm in diameter. These holes permitted gas to pass upward and particles to pass downward.

The depth of the lower fluidized bed was determined by the height of the overflow tube (0.86 m). The particles which passed out the overflow. tube were collected in a canister that was emptied at regular intervals. This was the “overflow product” and was the principal solid product.

The main body of the reactor was surrounded by an electric furnace for temperature control. However, the reactor cap was entirely outside of the furnace and was not insulated to limit the temperature of the cap and minimize corrosion of the stainless steel by sulfur dioxide. Excessive corrosion of the stainless steel can which held the upper fluidized bed

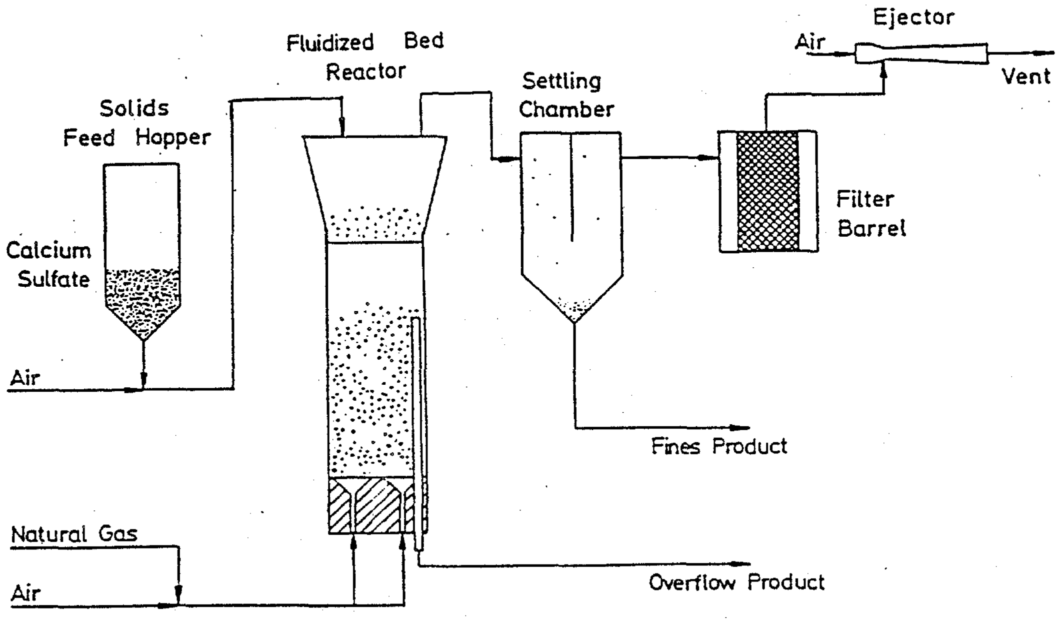

Figure 1. The bench-scale, two-stage fluidized bed system used for treating waste gypsum.

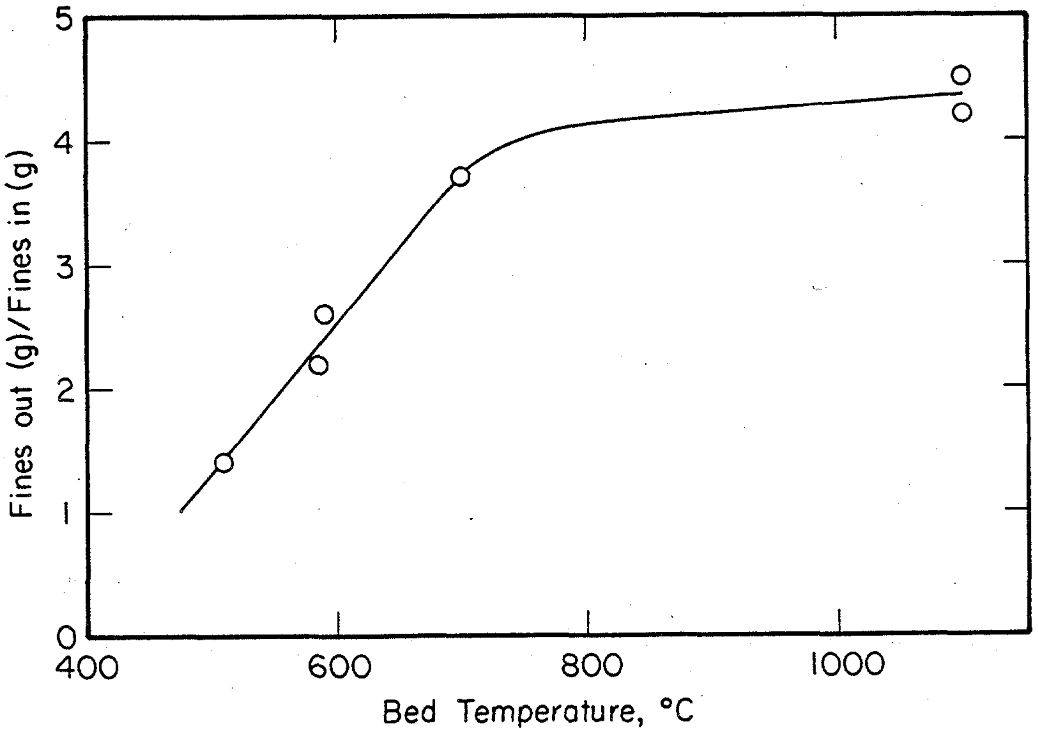

Figure 2. Effect of fluidized bed temperature on generation of fines.

was avoided by the cooling effect of the fresh feed which limited the temperature of the upper bed to a reasonable level.

An L-valve feeder supplied feed particles at a controlled rate, and the feed was conveyed pneumatically to the top of the reactor. Air and natural gas flow rates were measured with calibrated rotameters. The air flow was controlled manually and was kept constant throughout a given run. The natural gas flow was cycled on and off by a solenoid-operated valve which was controlled by an electric timer. During the portion of the cycle when gas was flowing, the gas flow rate was set by a manually operated needle valve.

The reactor off-gas was conducted through a large settling chamber to remove the bulk of the fines entrained in the reactor. The fines were collected in a canister which was emptied at regular intervals. The gas then passed through a filter made from a blanket of glass fibers to remove most of the remaining dust before being discharged through an ejector. The ejector was driven by compressed air and kept the off-gas handling system under reduced pressure to prevent escape of toxic gases.

Provision was made for withdrawing samples of off-gas from the top of the reactor for analysis. Samples were filtered and routinely analyzed with a standard Orsat apparatus to determine the relative concentrations of acidic gases, oxygen, and carbon monoxide.

FEED MATERIAL

For the runs described below, the reactor feed was waste gypsum produced by neutralizing acidic waste water with lime at the Radford Army Ammunition Plant in Radford, Virginia. The gypsum was precipitated in the form of very small crystals and recovered as a wet sludge. The material was dried and subsequently compacted by application of high pressure with a double-roll press. The compacted material was then crushed and separated with a double-deck vibrating screen to provide a feedstock largely composed of particles in the range from 0.42 to 1.68 mm.

REACTOR OPERATING PROCEDURE

The reactor was preheated overnight with the electric furnace to about 1000°C, and then air was passed through the hot reactor for several hours to preheat the off-gas handling system. After the system gas heated thoroughly, the reactor was filled gradually to the top of the overflow tube with fluidized material which had been reacted previously. After solids were passing freely out of the reactor overflow tube, the flow of natural gas was started, and the bed temperature rose rapidly. The feed was changed to fresh, unreacted material, and the desired operating conditions were soon established. Operating conditions were then kept constant to allow the system to approach steady-state. Although the natural gas flow was periodic in nature, both the average flow rate and cycle time were kept constant.

During the operation, the canisters which received solids issuing from the overflow tube and from the settling chamber were emptied periodically, and the solids were weighed and sampled for analysis. The reactor off-gas was sampled intermittently and analyzed with the Orsat apparatus. Most of the runs were continued for 5-6 hr or more, and results were reported for the final 1-2 hr when conditions appeared to approach a steady-state. After the operation was completed, the unit was shut down and allowed to cool to ambient temperature. The reactor was emptied and the system disassembled, cleaned, and prepared for the next run.

The conversion or percent desulfurization of the reacted particles was based on the compositions of the feed (F) and solid product (P) and was calculated by means of the following expression:

$$\text{Des.}(\%) = 100 - 100 \left[\frac{\%\text{Ca}}{\%\text{SO}_3}\right]_F \left[\frac{\%\text{SO}_3 + 2.5(\%\text{S}^=)}{\%\text{Ca}}\right]_P \qquad (5)$$

The sulfur dioxide concentration of the off-gas was estimated by applying a sulfur balance to the solids entering and leaving the reactor. A calcium balance was used to determine the percentage of calcium fed which was recovered in the solids that issued from the overflow tube and to estimate the yield of calcium oxide in this product.

EXPERIMENTAL RESULTS

It required a major effort to modify an existing bench-scale fluidized bed reactor for two-stage operation. The greatest hurdle was the transfer of material from the upper stage to the lower stage at a controlled rate. Several potential methods for transferring particles were tested in both a cold model and the heated reactor. The one which worked the best was the so-called weeping and dumping method. In this method the holes in the gas distributor for the upper stage were sufficient in size and number to allow particles to pass downward against the rising gas flow by weeping and/or dumping.

After satisfactory two-stage operation was achieved, the-series of runs listed in Table I was conducted. The depth of the upper fluidized

Table I. Runs made with the two-stage fluidized bed reactor using the cyclic mode of operation

Run No.	T-I	T-II	T-III	T-IV
Feed composition and size				
Calcium as Ca, %	24.5	24.5	24.5	24.5
Sulfate as SO_3, %	49.5	49.5	49.5	49.5
Moisture as H_2O, %	14.0	14.0	14.0	14.0
Size range, mm	0.4-1.7	0.4-1.7	0.4-1.7	0.4-1.7
Average feed rate, kg/hr	8.2	8.1	9.4	11.4
Overall mole N.G./mole $CaSO_4$	1.11	1.13	1.14	1.28
Overall mole air/mole $CaSO_4$	7.87	8.01	8.12	9.11
Upper fluid. bed temp., °C	510	585	590	700
Lower fluid. bed temp., °C	1100	1100	1100	1100
Max. superficial vel.,				
Upper bed, m/s	0.60	0.65	0.76	1.14
Lower bed, m/s	1.05	1.05	1.20	1.61
Min. superficial vel.				
Upper bed, m/s	0.45	0.34	0.59	0.88
Lower bed, m/s	0.80	0.79	0.93	1.24
Total cycle time, s	50	50	50	50
Reducing zone or phase				
Time interval, s	42	42	42	35
mole air/mol N.G.	6.0	6.0	6.0	5.0
Estimated SO_2 conc., %	8.0	7.9	7.6	6.5
Overflow product				
Desulfurization, %	93	90	86	86
Ca recovery, %	96	100	99	97
CaO yield, %	88	89	85	83
Fines entrained in off-gas				
Entrainment rate, kg/hr	0.12	0.13	0.14	0.25
Fraction entrained, %	39	35	26	38
Desulfurization, %	39	65	57	42
Sulfide content, $S^=$ %	--	--	--	--
Fines out (g)/fines in (g)	1.4	2.2	2.6	3.7

bed seemed to be controlled by the gas velocity. Although the gas velocity through the holes in the gas distributor was probably the controlling parameter, it was not possible to estimate this velocity with reasonable accuracy because the temperature of the gas passing through the holes was unknown. However, the superficial gas velocity in the upper and lower beds was estimated since the bed temperatures were measured. Minimum and maximum values of the velocity are listed in Table I. Minimum values were obtained during the oxidizing phase of each cycle when only air was fed, whereas maximum values were obtained during the reducing phase when both air and natural gas (N.G.) were supplied. For runs T-I to T-III the minimum gas velocity was relatively low, and consequently the depth of the upper fluidized bed was a minimum. For run T-IV the gas velocity was somewhat higher, and the depth of the upper fluidized bed was significantly greater which may account for the somewhat higher bed temperature observed during this run. In general, the overall results did not seem to be greatly affected by the depth of the upper bed.

To compare the results of the two-stage process with those of the single-stage process, data taken previously under similar conditions are included in Table II for the single-stage method. Runs S-I and S-II were based on the two-zone or zonal operating mode, whereas runs S-III and S-IV were based on the cyclic operating mode. The feed material and the feed rates were generally similar among the different runs except for run S-I and run T-IV where a somewhat larger feed rate was used. The temperature of the fluidized bed of reacting material was 1100°C in all cases, and the air-to-natural gas ratio in either the reducing zone or during the reducing phase was similar (4.5 to 6.4) among the various runs. On the other

Table II. Runs made with the single-stage fluidized bed reactor

Run No.	S-I	S-II	S-III	S-IV
Operating mode	Zonal	Zonal	Cyclic	Cyclic
Feed composition and size				
Calcium as Ca, %	25.6	26.6	24.7	24.5
Sulfate as SO_3, %	50.0	51.7	48.9	49.7
Moisture as H_2O, %	8.5	8.5	13.9	14.0
Size range, mm	0.4-1.7	0.4-1.7	0.6-1.7	0.6-1.7
Average feed rate, kg/hr	11.3	8.2	9.5	9.1
Overall mole N.G./mole $CaSO_4$	1.57	1.53	1.50	1.57
Overall mole air/mole $CaSO_4$	13.0	12.8	13.6	12.4
Fluid. bed temp., °C	1100	1100	1100	1100
Max. superficial vel., m/s	1.76	1.26	1.60	1.37
Total cycle time, sec.	n.a.	n.a.	50	50
Reducing zone or phase				
Time interval, s	n.a	n.a.	30	40
mole air/mole N.G.	5.0	4.5	5.4	6.4
Estimated SO_2 conc., %	5.4	5.7	4.6	5.6
Overflow product				
Desulfurization, %	95	98	91	97
Ca recovery, %	75	87	75	80
CaO yield, %	73	85	68	78
Fines entrained in off-gas				
Entrainment rate, kg/hr	1.24	0.46	0.73	0.62
Fraction entrained, %	94	88	98	--
Desulfurization, %	71	66	75	78
Sulfide content, $S^=$ %	0.3	0.2	1.9	2.3
Fines out (g)/fines in (g)	4.5	4.2	--	--

hand, due to the greater thermal efficiency of the two-stage process, the runs based on this method required significantly less fuel and air than those based on the single-stage method. Thus, the natural gas feed rate was 1.11 to 1.28 mole/mole $CaSO_4$ in runs T-I to T-IV compared to 1.50-1.57 mole/mole $CaSO_4$ in runs S-I to S-IV, and the air rate was 8-9 mole/mole $CaSO_4$ in runs T-I to T-IV compared to 12-13 mole/mole $CaSO_4$ in runs S-I to S-IV. As a consequence of the smaller fuel and air requirements for the two-stage process, the maximum superficial gas velocity was lower and the concentration of sulfur dioxide in the off-gas was higher for this process than for the single-stage process. Therefore, the concentration of sulfur dioxide was 7.6-8.0% for runs T-I to T-III compared to 4.6-5.7% for runs S-I to S-IV.

The lower gas velocity employed in the two-stage process as well as the design of the reactor led to a significantly smaller rate of particle entrainment in the reactor off-gas. For runs T-I to T-IV, the rate of entrainment was 0.12 to 0.25 kg/hr compared to 0.62 to 1.24 kg/hr for runs S-I to S-IV. For the two-stage process, the gas velocity in the upper stage was reduced by the lower temperature in this stage, and the velocity was reduced further in the freeboard section because of the increase in diameter of this section with height. For the two-stage process, all of the entrained fines were smaller than 0.42 mm as determined by dry screening (see Table III), and for the single-stage process at the same feed rate about 90% of the entrained material was smaller than this size.

An inspection of the particle size analysis data in Table III indicates that some particle decrepitation took place in the fluidized bed reactor. While the feed contained an appreciable amount of material in

Table III. Size distribution of feed and products for selected runs

Material	Size Range, mm	Size distribution, wt.% Run T-I	Run T-II	Run S-II
Feed	+1.68	0	0	2.0
	-1.68/+1.19	11.5	22.9	38.3
	-1.19/+0.84	44.2	42.8	40.0
	-0.84/+0.60	31.4	20.8	14.4
	-0.60/+0.42	7.8	9.6	2.8
	-0.42	5.1	3.9	2.5
Overflow Product	+1.68	0	0	0.1
	-1.68/+1.19	1.0	1.5	13.1
	-1.19/+0.84	35.0	39.0	42.0
	-0.84/+0.60	39.4	35.2	32.4
	-0.60/+0.42	19.6	18.4	10.7
	-0.42	5.0	5.9	1.7
Entrained Fines	+0.42	0	0	9.3
	-0.42/+0.30	2.9	1.5	20.8
	-0.30/+0.15	39.6	34.4	30.1
	-0.15/+0.074	32.7	32.9	21.1
	-0.074	24.8	31.2	18.7

the size range from 1.19 to 1.68 mm, the products had relatively little material in this size range. Therefore, the larger particles must have broken into smaller particles. To obtain a more quantitative assessment of the degree of decrepitation and entrainment, a calcium material balance was applied to the -0.42 mm size particles or fines. The amount of calcium in the fines which were either entrained in the off-gas or recovered in the overflow product was determined and compared with the amount of calcium in the fines contained in the feed. This determination provided the ratio (fines out/fines in) reported in Tables I and II. For runs T-I to T-IV this ratio was significantly less than for runs S-I and S-II indicating that the production of fines was much lower in the two-stage process than in the single-stage process. A plot of the ratio against the temperature of the fluidized bed first seen by the feed produced the very interesting correlation shown in Figure 2. This diagram shows that the production of fines was closely related to bed temperature which suggests that decrepitation was due largely to thermal shock.

The quantity of calcium contained in the entrained fines was divided by the quantity contained in the fines which were either entrained or recovered with the overflow product, and this ratio is reported as "fraction entrained" in Tables I and II. For runs T-I to T-IV, the fraction entrained was 26-39%, whereas for runs S-I to S-III it was 88-98%.

From the preceding discussion it is apparent that the two-stage process not only produced fewer fines than the single-stage process but also retained more of the fines in the overflow product. Consequently, both the recovery of calcium and yield of calcium oxide in the overflow product were greater for the two-stage process than for the single-stage process. This is an important advantage for the two-stage process since entrained fines were not reacted as completely as the overflow product, and in an industrial application the entrained fines would need to be recycled and reincorporated in the feed which would reduce operating and thermal efficiencies.

While the results of the two-stage operation were superior to those of the single-stage operation in most respects, the desulfurization of the solids was slightly greater for the single-stage operation. The lower desulfurization achieved in the two-stage operation may have been a result of the weeping and dumping method of particle transfer between stages. Some of the particles which rained down from the upper stage probably fell directly into the overflow pipe from the second stage without having an opportunity to react. This problem would be easily overcome in a larger reactor.

CONCLUSIONS

A two-stage fluidized bed process was demonstrated for decomposing calcium sulfate into sulfur dioxide and quicklime. Feed particles were preheated in the first stage and subsequently reacted at a higher temperature in the second stage by treatment with a mixture of gases which was alternately reducing and oxidizing. Preheating was accomplished by contacting the feed with the hot off-gas from the second stage. Since the preheating stage was located directly above the reaction stage, it proved possible to transfer particles from the upper to the lower stage by weeping and dumping particles through holes in the plate separating the two stages.

The results achieved with the two-stage process were superior in most respects to those achieved previously with a single-stage process under generally similar conditions. Because of the greater thermal efficiency of the two-stage process, the fuel and air requirements were lower and the superficial gas velocity in the reactor was lower. The superficial gas velocity in the upper stage was further reduced by the lower temperature prevailing in this stage, and the velocity was reduced even further in the freeboard section above the bed due to the expanded diameter of this section. As a consequence of the lower superficial velocity, the rate of entrainment of fines was smaller for the two-stage process. In addition, fewer fines were produced in the two-stage process, probably because the feed experienced less thermal shock when it was introduced into the preheating stage having a temperature of 500-700°C rather than directly into the reaction stage at 1100°C. Consequently the yield of calcium oxide in the solid product and the concentration of sulfur dioxide in the gaseous product were higher for the two-stage process than for the single-stage process.

ACKNOWLEDGEMENTS

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ABSTRACT

The search for a method of recycling phosphogypsum or for a beneficial use for the material has been one of the main concerns of the phosphoric acid industry for many years. It is indeed a paradox that phosphoric acid processes are designed to manufacture gypsum - about twice as much gypsum is produced as fertilizer products are - and yet most of the gypsum is discarded in a waste pile.

Consolidated Minerals, Inc. has concluded that integration of a power plant and a cement plant, with a phosphate mine and a fertilizer plant would create the necessary economics to make the recycling of phosphogypsum to cement and sulfuric acid feasible.

The main advantages of an integrated industrial complex are in reduced total costs and in waste utilization. For example, the power plant will incur much of the infrastructure cost, reducing capital investment costs on the other facilities when compared with stand-alone plants. Perhaps the most important savings allowed by integration are process related. In the Pine Level project, wastes from one plant become raw materials for another plant. About 85% of the raw materials required to make cement are recycled wastes from other plants.

In designing the overall concept, Bromwell & Carrier had to deal with the question of the radium content in phosphogypsum. Typical phosphogypsum contains an equivalent of 25-30 pCi/g of

radium-226. Materials of construction are presently limited to 10 PCi/g. Since it takes about 2 tons of gypsum to produce 1 ton of Portland cement, the Ra-226 content in phosphogypsum would have to be less than 5 pCi/g to produce an acceptable cement. The specification of a recyclable gypsum for cement manufacture is a gypsum containing less than 0.5% total P_2O_5, less than 0.1% F and less than 5 pCi/g of Ra-226.

In addition to those objectives, Bromwell & Carrier sought to develop a process to use a low-grade, partially beneficiated rock in order to extend reserves and reduce rock processing costs. The result is the Ecophos® process. The essential features of this new gypsum and phosphoric acid process are:

1. The Ecophos® process accepts a low-grade phosphate feed and is flexible over a wide range of rock qualities.

2. The clean gypsum produced meets and exceeds the requirements for cement manufacture. It is a snow-white, practically pure gypsum, which can be processed directly into Portland cement without further cleaning.

3. P205 recoveries are equal to or better than those of conventional dihydrate phosphoric acid processes.

INTRODUCTION

The search for a method of recycling phosphogypsum or for a beneficial use for the material has been one of the main concerns of the phosphoric acid industry.

It is indeed a paradox that phosphoric acid processes are designed to manufacture gypsum - about twice as much gypsum is produced as fertilizer products are - and yet most of the gypsum is discarded into the ocean or in a waste pile.

In the United States, agricultural use is probably the most developed market for phosphogypsum. Use as a road base material is a promising large-scale future use for phosphogypsum in Florida. The above uses are not likely to generate significant income for the Florida phosphate industry, however.

The idea of using phosphogypsum as a raw material for cement faced the obstacle of several established paradigms.

The first one has to do with sulfur prices. Use of phosphogypsum as a source of sulfur for sulfuric acid plants might not be competitive with existing sources of sulfur.

The second questions the adequacy of the raw material. Since natural gypsum is clean, abundant, available and cheaper than clean phosphogypsum, using phosphogypsum would never be feasible. Besides, phosphogypsum could "never" be as pure as natural gypsum.

Finally, there is the question of the radium content in phosphogypsum. Typical Central Florida phosphogypsum contains an equivalent of 25-30 pCi/g of Ra-226. The radium-226 disintegrates, producing Radon gas. Exposure to high levels of radon has been related to lung cancer. The Ra-226 content in materials of construction is presently limited to 10 pCi/g in the U.S. Since it takes about 2 ton of gypsum to produce 1 ton of cement, the Ra-226 content in phosphogypsum would have to be less than 5 pCi/g.

Perhaps for such reasons, a phosphogypsum to cement and sulfuric acid project has not been seriously proposed in Florida in the past.

The first proposal to do so is the Pine Level Project. What makes the Pine Level Project different is the integration of a coal-fired power plant, a cement plant, the phosphate mine and the phosphate products plant (Figure 1).

This integration is the key for the economic feasibility of a cement-sulfuric acid type of sulfur recycle process. It is significant that such concept was proposed by a company active in the coal-fired power, cement and phosphate industries. This concept is now being developed by Bromwell & Carrier, Inc., a professional engineering company specialized at finding innovative solutions for complex problems.

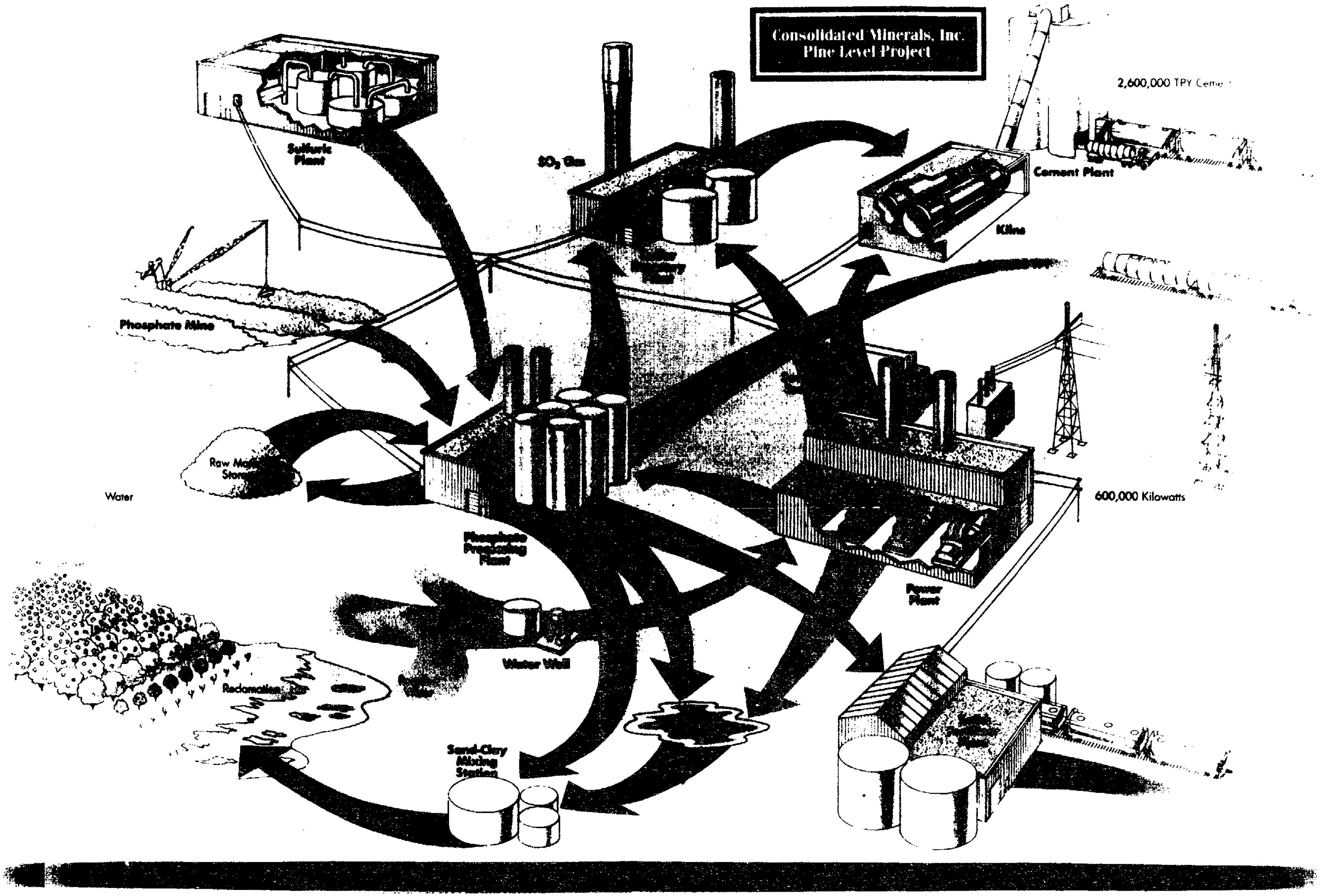

Figure 1. Pine Level Project Conceptual Flowsheet

Table I

Pine Level Project Capacities

System	Capacity
Power Plant	660 MW, coal-fired
Mine	20 million ton per year of matrix
Phosphate Products	5 million ton per year of pre-concentrate
	1.1 million ton P2O5 per year of fertilizer products
Cement	2.6 million ton per year of Portland cement
Sulfur recycle	1 million ton per year of sulfur equivalent recycled

The second key to the feasibility of the Pine Level Project is Ecophos®. The gypsum produced by Ecophos® meets and exceeds the criteria for recyclability. In fact, the gypsum is so pure that Ecophos® redefines phosphogypsum.

This paper will describe those two keys to the Pine Level Project: how integration and Ecophos® make the project feasible.

ADVANTAGES OF INTEGRATION

Integration can be analyzed from the vantages of capital costs and operating costs. The Pine Level Project capital cost has been estimated at about $900 million (in 1990 values). The major capital savings allowed by the integrated design are in the areas of:

1. Transportation. The power plant absorbs the infrastructure cost for transportation, roads and

railroad. Such infrastructure developed for stand-alone cement, power, mine and phosphate plants would cost approximately $120 million additional.

2. Energy. The power plant absorbs the cost of coal operations (procurement, handling, storage, etc.) as well as most of the cost of the electrical network. If the coal-handling facilities would have to be duplicated for a cement plant (coal-fired kilns), the cost would be approximately $20 million additional.

3. Other infrastructure. Savings in the other common infrastructure for the integrated complex are estimated to be approximately $160 million.

All told, there are an estimated $300 million in capital costs saved through integration.

Table II

Order of Magnitude Capital Costs Saved Through Integration in The Pine Level Project

	$ millions
Transportation Infrastructure	120
Energy Infrastructure	20
Other Infrastructure	160
Total	300

Perhaps the most important savings allowed by integration are process related. In the Pine Level project, wastes from one plant become raw materials for another plant. Extensive water recycling is possible.

About 80% of the raw materials for the manufacture of cement are provided by would-be wastes from stand alone power and phosphate plants. Also, about 80% of the sulfur is provided by recycled raw materials (Table III).

Table III

Use of Process Waste Materials Allowed by Integration in The Pine Level Project

Wastes used by the Cement Plant	Volume, ton/year
Power plant fly ash	250,000
Power plant flue gas scrubber effluent	460,000
Gypsum from phosphate plants	3,500,000
Sulfur recycle equivalent	**ton S /Year**
From FGD Scrubber	80,000
From gypsum	640,000

The other important advantage due to integration is reflected in the water balance, both clean water supply and water discharge. The current design, which intensively recycles water, shows that the mine, power plant, cement plant and chemical plant will consume approximately the same amount of make-up water as would a mine and beneficiation plant above.

Similarly, a stand-alone grouping of plants might be expected to discharge 3,000-4,000 gpm of cooling tower blowdown, demineralizer regenerant, etc. The Pine Level complex is designed so that each unit consumes another unit's waste water, thus permitting a "zero-discharge" design (Table IV).

Table IV

Magnitude of Water Recycling in The Pine Level Project

	gpm
Water Import	
Mine and Beneficiation Only	8,900
Integrated Complex	8,900
Water Discharge	
Stand-alone Plants	3,000-4,000
Integrated Complex	zero

ECOPHOS®

The second fundamental factor affecting the feasibility of the Pine Level Project is the ability to produce a recyclable gypsum. The definition of a recyclable gypsum for cement manufacture is a gypsum containing less than 0.5% total P_2O_5, less than 0.1% F and less than 5 pCi/g of Ra-226.

In addition to those objectives, Bromwell & Carrier sought to develop a process to use a low-grade, partially beneficiated rock in order to extend the reserves and reduce processing costs. This approach to in fact integrate the mining with the chemical plant has been long pursued by the industry.

We note in passing that the Pine Level deposit contains three distinct ore bodies; a Bone Valley layer, a Lower Pleistocene layer and a Hawthorn layer. The mining plan and mine design are really "three-in-one". Because the rock quality will vary the ability of the chemical plant to handle a low-grade rock is very important for this project.

Bromwell & Carrier is presently seeking patents for the Ecophos® process. Therefore we are not prepared to disclose full process details at this moment. The essential features are:

1. The Ecophos® process accepts a low-grade phosphate feed and is flexible over a wide range of rock quality.

2. The clean gypsum produced meets and exceeds the requirements for cement manufacture and could have many higher value usages (see Table V). It is much purer than natural gypsum.

3. P_2O_5 recoveries are equal to or better than those of conventional dihydrate phosphoric acid processes (see Table V).

Table V

Composition of the Gypsum Produced by the Ecophos® Process

	%, dry basis
Total P_2O_5	< 0.5
F	0.02
CaO	31.6
SO_4	55.8
Fe_2O_3	0.02
Al_2O_3	0.04
MgO	0.02
Ra-226	< 2 pCi/g

Although there is an important economic incentive to convert gypsum to cement in the Pine Level Project, we have sought to produce a gypsum which could have even more profitable usages. The purity of the gypsum produced by Ecophos® is higher than that of natural gypsum or of other by-product gypsum such as flue gas desulfurization sludge gypsum. Inevitably new markets and products will be created to take advantage of the new material.

Table VI

P_2O_5 losses in the Ecophos® process

	% of rock P_2O_5
water soluble	< 1.0
citrate soluble	< 0.5
citrate insoluble	< 0.5
total	< 2.0

CONCLUSION

The Pine Level Project is an integrated industrial complex comprising a power plant, a cement plant, a phosphate mine and a phosphate products plant. The integration creates the economic conditions for the feasibility of sulfur recycle in the form of gypsum to cement and sulfuric acid processes.

Starting from a low grade rock, the Ecophos® gypsum-phosphoric acid process yields a clean, pure, snow-white gypsum which can be processed directly into Portland cement without further cleaning (Figure 2).

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Figure 2. Photo of Conventional PhosphoGypsum and CMI Gypsum

EFFECTS OF PHOSPHOGYPSUM AND OTHER SOIL, AMENDMENTS ON CITRUS GROWTH, PHYTOPHTHORA FOOT ROT AND SOIL MICROFLORA

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ABSTRACT

At each of three Florida flatwoods groves, all over 12 years old, phosphogypsum was applied at 0, 560, 1120, and 2240 kg-ha^{-1} and commercial gypsum at 2240 kg·ha^{-1} in March 1986 and March 1987. Rhizosphere and nonrhizosphere soils sampled for populations of Fusarium spp., Streptomyces spp., and Phytophthora spp. indicated that treatment differences occurred but that differences did not suggest trends or shifts in populations among treatments. No treatment caused a significant reduction in populations compared with the control. Flats of Astatula fine sand were amended with humate, phosphoclay, and phosphogypsum (990 g each ·165 kg^{-1} sand) in the greenhouse and inoculated with F. solani. Inoculation in the phosphogypsum treatment caused a 50% reduction in rough lemon seedlings planted as seed to the flats. Within the same soil amendment, seedling height differed only between the humate control and inoculated flats.

There was an inverse relationship between populations of *F. solani* and fluorescent pseudomonads in phosphogypsum-amended and *F. solani*-inoculated and control soils. In two soils amended with phosphogypsum (17,621 $kg \cdot ha^{-1}$) phosphoclay (16,200 $kg \cdot ha^{-1}$), and humate (16,200 $kg \cdot ha^{-1}$) in a greenhouse study, lowest root rot and lowest phytophthora-infected roots occurred in the phosphogypsum treatment of both soils. Field and greenhouse results suggest that phosphogypsum effects are on the tree rather than the fungus.

INTRODUCTION

Most Florida citrus soils are sandy, slightly acidic, and have poor water-holding and cation-exchange capacities (11). In such soils, citrus roots are exposed to greater environmental fluctuations and to more frequent cycles of stress (9). Soilborne, plant pathogenic fungi in such soils are affected by fewer competitors than in soils containing moderate to high levels of organic matter. The soils and climate of Florida are favorable for wilt diseases caused by root-rotting fungi, and wilt symptoms are also generally more severe in warm climates (3).

The two most common root disease fungi infecting citrus in Florida, *Fusarium solani* (Mort.) Appel & Wr. emend. synd. Hans. and *Phytophthora parasitica* host., are affected by soils, and diseases they cause can be suppressed in certain soils. Soils that are suppressive to *Phytophthora* spp. contain high levels of organic matter and exchangeable calcium (5). Disease symptoms caused by Fusaria are either reduced or absent in disease-suppressive soils. Soils rich in clay, predominantly montmorillonite clay, possess characteristics disease-suppressive (1, 14) to Fusaria. No citrus soils naturally suppressive to Fusarium and Phytophthora have been identified and only a few areas in Florida, principally in the flatwoods, contain high organic matter and calcium. Florida soils contain only traces of clay and the kaolinitic type is predominate, which is typical of subtropical and tropical regions (11).

The use of soil amendments to modify soils and their microflora to enhance citrus plant and root health has been investigated in Florida. In two new plantings established at Ft. Pierce and Ft. Meade on different soil types, phosphogypsum, phosphoclay, peat, humate, and calcitic limestone were deep-tilled at single rates into the soil prior to planting. Phosphogypsum and phosphoclay, common by-products of phosphate mining in Florida, are readily available and inexpensive sources of calcium and clay. During the first year after planting at Ft. Pierce, none of the amendments applied influenced foot rot caused by _P. parasitica_ or populations of fluorescent _Pseudomonas_ spp. in rhizosphere and nonrhizosphere soils (7). Also, there were no consistent trends in the populations of rhizosphere and nonrhizosphere total fungi or _Streptomyces_ spp. or in the incidence of root-infecting fungi by soil mixing or adding amendments at these two locations. _Fusarium solani_ was the fungus most frequently isolated from roots (12). Humate applied to soil around citrus trees under stress, in another study, resulted in increased numbers and extent of growth flushes, as well as increased fruit set and production compared with controls (16).

In other areas of the country, some of the same amendments promoted favorable responses in crop growth and repressed soilborne, plant-pathogenic fungi. Lime and gypsum treatments to soil planted to pea reduced propagule density of _F. solani_ f. sp. _pisi_ after the midbloom stage (2). Application of gypsum to peanut field plots caused a significant decrease in the isolation frequency of F. solani from seed between zero gypsum and 560 kg·ha^{-1} and between 560 and 1680 kg·ha^{-1} (4). Gypsum also reduced pot rot of peanuts (15).

As part of a project to determine effects of phosphogypsum on citrus trees, soil in three mature groves was treated with this amendment. Treatment effects on yield, juice quality and radionucleide content, and on tree condition were parameters evaluated in these groves and constitute material presented by the junior author of this paper in a companion presentation in this symposium. In this study, populations of soil microflora were assessed in these groves. In addition, effects of amendments on citrus growth and disease incidence by F. solani and P. parasitica were determined in the greenhouse.

MATERIALS AND METHODS

Soil Amendments Applied to Mature Groves

Three mature groves in the flatwoods were selected to represent two typical soil series. They included Myakka (aeric haplaquods) and Smyrna (aeric haplaquods) fine sands from DeSoto County near Arcadia, and Oldsmar (alfic arenic haplaquods) fine sand from St. Lucie County near Ft. Pierce. Citrus scion-rootstocks were 20-year-old Hamlin sweet orange (Citrus sinensis (L.) Osb.) on Cleopatra mandarin (C. reticulata Blanco) rootstock on the Myakka soil; 12-year-old Hamlin on sour orange (C. aurantium L.) rootstock on the Smyrna soil, and 25-year-old Hamlin on Cleopatra mandarin on the Oldsmar soil.

At each of the three sites, phosphogypsum was applied by hand at 0, 560, 1120, and 2240 kg·ha^{-1} and commercial gypsum at 2240 kg·ha^{-1}. A completely randomized design with four replications of each treatment, was used in each grove. Each replicate contained eight trees. Amendments were applied annually to the soil surface under each tree in March 1986 and March 1987. Soil and root samples were collected from the first 0.3 m of soil, four locations around each tree, on June 8, 1987, from the Myakka soil, on July 1, 1987, from the

Oldsmar soil, and on July 27, 1987, from the Smyrna soil. Rhizosphere and nonrhizosphere soils were analyzed for *Fusarium* spp., *Streptomyces* spp. and *Phytophthora* spp. colony-forming units (cfu) per gram soil using methods defined by Smith, et al. (12).

A third application of the amendment treatments was made on July 15, 1988, to the Oldsmar soil. Roots were collected in the manner described above from the control and 2240 $kg \cdot ha^{-1}$ phosphogypsum treatments just prior to application and again on August 15, 1988. Rhizosphere populations of *Streptomyces* spp. and fluorescent pseudomonads were assessed. Fluorescent pseudomonads were detected using methods described by Gould et al. (7). Soil samples were collected from the first 30 cm of soil four equidistant locations around each tree and analyzed for S and Ca content. Calcium was extracted from soil using 1 M KCl and S was extracted with 0.08 M $CaH_4(PO_4)_2H_2O$ by, Agro Services International, Inc., Orange City, Florida.

On March 17, 1989, a fourth application of the same treatments was applied to different trees in the vicinity of the previously treated trees on the Oldsmar soil. Four trees were treated with each amendment rate. Beginning the middle of April and for each month through August, soil samples were collected from the first 30 cm of soil in at least 10 locations under each tree. Soils were analyzed for Ca and S in the manner described previously. Rainfall data representative of this area were collected in 1987 and 1989 by the Ft. Pierce Agricultural Research and Education Center located about 8 km from the grove.

Greenhouse Studies

Effects of Amendments on Plant Growth, *Fusarium* spp. and Fluorescent Pseudomonads

In August 1986, twenty-four 48 X 35 X 27 cm wooden flats were filled to within 4 to 5 cm of the top with amended steam-pasteurized Astatula fine sand (hyperthermic uncoated typic quartzipsamments). All soil was amended with phosphorus (P) from a source of superphosphate to bring soil P to a level of 210 ppm, considered adequate for plant growth. Soil in 18 flats was mixed with three amendments, six with phosphoclay, six with phosphogypsum, and six with humate, each at 990 g of amendment to 165 kg^{-1} soil. Six flats containing soil mixed with P were used as controls. Three flats of each soil treatment were inoculated with a 300-ml aqueous suspension containing 6.7 X 10^{6} spores of _F. solani_ per ml on August 19. All flats were planted with 50 rough lemon plants (_Citrus limon_ (L.) Burm. f.) per flat on August 18. Data were collected on seedling stand, and 10 plants per flat were rated for seedling height on November 15. Roots of these 10 seedlings were scored for root rot using a rating of 0 to 5. Plants were scored a zero if there was no visible epidermal and cortical sloughing and five was assigned if extensive root rot was evident. _Fusarium_ spp. and fluorescent pseudomonad cfu were quantified per flat using the methods previously described.

Effects of Amendments on Plant Growth and Phytophthora Foot Rot

Two citrus soils, one from the Ft. Pierce IFAS station (Wabasso sand, a sandy siliceous, hyperthermic alfic haplaquods) and another from a grove near Indiantown (unidentified), were amended with 17,621 kg·ha^{-1} phosphogypse, 16,200 kg·ha^{-1} phosphoclay, and 16,200 kg·ha^{-1} humate. Plants were fertilized monthly with a liquid 15-7-7 fertilizer. In November 1987, plants were scored for shoot and root dry weight, veinal chlorosis, foot rot, root rot, and roots colonized by Phytophthora. In addition, four root pieces per pot were plated on PAPPH medium (13) to detect Phytophthora.

Laboratory Study

Effect of Phosphoclay and Phosphogypsum on Growth of *Phytophthora parasitica*

Corn meal agar (CMA) was amended with 0.0, 0.01, 0.05, 0.10, and 1.0% phosphoclay and phosphogypsum and poured into petri plates. Five-mm-diameter CMA plugs of a 7-day-old *P. parasitica* isolate grown in petri plates were transferred to the CMA containing the amendments. One plug was transferred to five replicate plates of each amendment treatment. Colony diameter was measured 8 days after transfer.

RESULTS

Soil Amendments Applied to Mature Groves

In all three soils sampled, significant differences between phosphogypsum treatment in rhizosphere and nonrhizosphere microflora cfu of species of *Fusarium, Streptomyces*, and *Phytophthora* occurred, but these differences did not suggest trends or shifts in populations among treatments (Tables 1-3). The source of the gypsum, whether phosphogypsum or commercial gypsum, did not affect microflora cfu in any of the soils tested (Tables 1-3). In all three soils, no amendment treatment significantly reduced microflora cfu compared with the control. As expected from previous research (10), almost all Fusarium cfu were *F. solani*. Rainfall from March 1 through August 1989 was 21.66 inches, and 21.59 inches for those months in 1987.

Although soil samples were collected for mineral analyses from each of the three groves at the time roots were collected, the soils were misplaced, Soils were collected from the Oldsmar site in 1989 for the purpose of determining Ca and S distribution during the same period of the year when soil microflora data were determined. Data indicated that S gradually decreased during the growing season (Figure 1), and soil S increased as the rate of phosphogypsum increased. Soil Ca also increased as the rate of phosphogypsum increased (Figure 2); but during the growing season, Ca levels were generally stable.

In the Oldsmar fine sand in 1988, fluorescent pseudomonads naturally declined in August compared with July, and each month populations were not significantly affected by phosphogypsum. No differences occurred in *Streptomyces* spp. cfu after applying phosphogypsum (Table 4). No significant change in Ca occurred between each treatment and each sampling date (Table 4). Soil S did not differ between these two treatments on July 13; but on August 15, S was significantly higher in the phosphogypsum treatment than in the control (Table 4).

Greenhouse Studies

Effects of Amendments on Plant Growth, *Fusarium* spp. and Fluorescent Pseudomonads

In flats containing soil modified with amendments and inoculated with *F. solani*, twice as many seedlings grew in the phosphogypsum control as in the inoculated flats (Table 5), but height of these seedlings did not differ between these treatments. Humate reduced seedling height more than other amendments but seedlings were taller in inoculated humate than the control. *Fusarium* spp. cfu were consistently higher in flats amended with *F. solani*, but flats amended with phosphoclay and the fungus had the lowest number of cfu and this may be due to the clay component of this amendment (Table 6). In phosphogypsum-amended soil inoculated with *F. solani* and in the control, there was an inverse relationship between populations of *F. solani* and fluorescent pseudomonads (Table 6). *F. solani* did not cause obvious root rot symptoms on plants in inoculated flats and no root rot was apparent on control plants. Humate had the strongest depressive effect on plant growth and fluorescent pseudomonad development.

Effects of Amendments on Plant Growth and Phytophthora Foot Rot

In the Ft. Pierce soil, phosphoclay and humate exerted a depressive effect on plant dry matter, and all three amendments significantly depressed root dry weight compared with the control (Table 7). None of the amendments were suppressive to plant growth in the Indiantown soil. *Phytophthora parasitica* caused foot rot and root rot in both soils and these symptoms caused interveinal chlorosis in leaves. No treatments affected foot rot in either soil. Treatments affected root rot development in the Indiantown soil, but not in the Ft. Pierce soil. Phosphogypsum significantly reduced colonization of roots by Phytophthora in the Indiantown soil.

Effect of Phosphoclay and Phosphogypsum on *Phytophthora parasitica* Growth in the Laboratory

Phosphoclay had no suppressive nor stimulatory effect on *P. parasitica* growth (Table 8), and only the highest rate of phosphogypsum affected growth of this fungus (Table 8).

DISCUSSION

The reduction in *F. solani* populations noted in pea (2) and peanut (4) soils amended with lime and gypsum did not occur in the present study. If Ca was the principal factor responsible for reducing *F. solani* in pea and peanut soils, Ca in the field soils of this test should have been high enough throughout the summer to effect such a change. Providing that other cultural practices were the same, Ca content of the Oldsmar test soil should have been similar in 1987 and 1989 because rainfall data were the same both years. However, because Ca levels were similar between treatments in the 1989 sampling of the Oldsmar soil, there may not have been enough of a difference in Ca content in the different treatments to cause a significant change in microflora populations in 1987. Both fluorescent pseudomonads (8) and *Streptomyces* spp. (6) exhibit antagonistic activity against Fusaria, but they were not changed in soil treated with phosphogypsum in 1988 nor were *Streptomyces* spp. in 1987. Some improvement in tree health in the treated field soils (see Myhre, Martin, and Nemec paper in this symposium) implies, based on the absence of differences in soil microflora population data, that the improvement was due to nutritional reasons.

Neither phosphogypsum nor commercial gypsum had an influence on phytophthora populations in amended field soils. The only effect phosphogypsum exerted on *P. parasitica* in the laboratory was at a concentration higher than would be recommended for fertilizer use. However, phytophthora populations were generally low in these soils and may not have been potentially high enough to be a significant factor in disease development. No obvious increase or decrease in foot rot symptoms occurred on trees in these groves during the course of the tests.

In the greenhouse flat study, interesting interactions occurred in phosphogypsum-amended soil. *Fusarium solani*, although not causing root rot in rough lemon seedlings, was associated with a significant reduction in seedling stand in inoculum-amended flats and may have caused a reduction in the population of fluorescent pseudomonads. An effect of a pathogen on other soil microflora is not unexpected. In groves with blight symptoms, rhizosphere to soil populations of *Pseudomonas* spp. declined as symptoms increased but rhizosphere to soil populations of *F. solani* increased as symptom development increased (10), and this may have been due to an interaction between these two organisms. It is difficult to explain why in the flat study, a shift in. pseudomonads did not occur in the other amendment treatments.

In the greenhouse study with Ft. Pierce and Indiantown soils, there was a significant reduction of phytophthora-infected roots in the phosphogypsum-amended Indiantown soil and a generally lower root rot index in both soils. This is evidence that phosphogypsum may have had a direct effect on the fungus, which is not supported by data in the laboratory and field studies; or the phosphogypsum may have affected plant nutrition in such a way to depress development of the fungus on roots. This latter hypothesis is supported with data from another citrus grove soil amendment study near St. Cloud, Fla. There, significantly less phytophthora foot rot (8.3%) occurred in a gypsum treatment compared to the control (29.2%) [unpublished data]. Evidently, gypsum and phosphogypsum effects are on the tree rather than being the causal agent of foot rot.

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Table 1. Microflora propagules in rhizosphere and nonrhizosphere soil of citrus amended with three levels of phosphogypsum and one level of commercial gypsum at Arcadia, Florida (Myakka fine sand).

Treatments		Log^{10} (cfu/g)[z]	
($\text{kg}\cdot\text{ha}^{-1}$)	*Fusarium* spp.	*Streptomyces* spp.	*Phytophthora* spp.
Rhizosphere			
560, Phosphogypsum	4.3 a[y]	6.0 ab	1.3 a
1120, Phosphogypsum	4.5 a	5.6 b	0.0 b
2240, Phosphogypsum	4.3 a	6.0 ab	0.0 b
2240, Commercial gypsum	4.4 a	6.2 a	0.4 b
Control	4.5 a	6.1 ab	0.0 b
Nonrhizosphere			
560, Phosphogypsum	3.8 a	5.5 ab	0.6 a
1120, Phosphogypsum	3.8 a	5.6 ab	0.3 a
2240, Phosphogypsum	3.9 a	5.7 a	0.7 a
2240, Commercial gypsum	3.9 a	5.6 ab	0.3 a
Control	3.9 a	5.5 a	0.3 a

[z] Colony-forming units/gm soil. Zero values indicated cfu at nondetectable levels.

[y] Means in a column for rhizosphere soil and for nonrhizosphere soil followed by the same small letter are not significantly different at $P = 0.05$ by Duncan's multiple range test.

Table 2. Microflora propagules in rhizosphere and nonrhizosphere soils of citrus amended with three levels of phosphogypsum and one level of commercial gypsum at Ft. Pierce, Florida (Oldsmar fine sand).

Treatments ($kg \cdot ha^{-1}$)	Log^{10} (cfu/g)^z *Fusarium* spp.	*Streptomyces* spp.	*Phytophthora* spp.
Rhizosphere			
560, Phosphogypsum	1.5 b^y	6.5 a	0.0 a
1120, Phosphogypsum	1.8 a	6.7 a	1.7 a
2240, Phosphogypsum	2.1 a	6.7 a	0.0 a
2240, Commercial gypsum	1.8 ab	6.4 a	0.5 a
Control	1.9 ab	5.2 a	1.3 a
Nonrhizosphere			
560, Phosphogypsum	3.7 ab	5.3 a	0.7 a
1120, Phosphogypsum	3.8 a	5.3 a	1.1 a
2240, Phosphogypsum	3.7 ab	5.3 a	0.6 a
2240, Commercial gypsum	3.6 b	5.3 a	0.4 a
Control	3.6 ab	5.3 a	0.8 a

[z] Colony-forming units/gm soil. Zero values indicated cfu at nondetectable levels.

[Y] Means in a column for rhizosphere soil and for nonrhizosphere soil followed by the same small letter are not significantly different at P = 0.05 by Duncan's multiple range test.

Table 3. Microflora propagules in rhizosphere and nonrhizosphere soils of citrus amended with three levels of phosphogypsum and one level of commercial gypsum at Arcadia, Florida (Smyrna fine sand).

Treatments (kg·ha^{-1})	Log^{10} (cfu/g)^{z}		
	Fusarium spp.	*Streptomyces* spp.	*Phytophthora* spp.
Rhizosphere			
560, Phosphogypsum	4.7 b^{y}	6.2 a	0.0 a
1120, Phosphogypsum	5.1 a	6.2 a	0.5 a
2240, Phosphogypsum	4.7 b	6.2 a	0.0 a
2240, Commercial gypsum	4.5 b	6.0 a	0.0 a
Control	4.4 b	6.3 a	0.4 a
Nonrhizosphere			
560, Phosphogypsum	3.6 b	0.7 a	0.6 a
1120, Phosphogypsum	3.3 a	0.7 a	0.6 a
2240, Phosphogypsum	3.6 ab	0.7 a	0.3 a
2240, Commercial gypsum	3.6 ab	0.7 a	0.8 a
Control	3.6 ab	0.7 a	1.0 a

[z] Colony-forming units/gm soil. Zero values indicated cfu at nondetectable levels.

[y] Means in a column for rhizosphere soil and for nonrhizosphere soil followed by the same small letter are not significantly different at *P* = 0.05 by Duncan's multiple range test.

Table 4. Fluorescent pseudomonad and Streptomyces spp. colony-forming units (cfu) per gram rhizosphere soil and soil Ca and S of 2240 kg·ha^{-1} phosphogypsum treatment and control in the Oldsmar fine sand, Ft. Pierce, FL.

	Log^{10} (cfu/g)^{z}		Ca and S	
Treatments (kg·ha^{-1}) and sampling date^{y}	Fluorescent pseudomonads	Streptomyces spp.	Ca (meq/100 g)	S (µg/g)
July 13, 1988				
Control	7.3 a	7.1 a	5.2 a	58.9 a
2240, Phosphogypsum	7.3 a	7.3 a	5.1 a	77.4 a
August 15, 1989				
Control	6.9 ab	7.2 a	5.1 a	36.3 a
2240, Phosphogypsum	6.7 b	7.1 a	6.1 a	103.0 a

[z] Colony-forming units/gm soil.

[y] Treatment means both dates not sharing the same small letter are significantly different from one another according to Duncan's multiple range test at P = 0.05.

Table 5. Effect of soil amendments on greenhouse-grown rough lemon seedlings, final stand and height as effected by inoculation with _Fusarium solani_.

	Seedling stand			Seedling height		
Amendment[z]	Inoculated	Uninoculated		Inoculated	Uninoculated	
Humate	19.7 ± 4.9[y] ab[x]	18.0 ± 4.6 b	ns[w]	9.2 ± 2.0[y] c	8.4 ± 0.9 b	*[w]
Phosphoclay	25.7 ± 5.7 a	20.0 ± 1.7 b	ns	21.7 ± 1.6 a	20.3 ± 2.1 a	ns
Phosphogypsum	14.3 ± 3.1 b	29.0 ± 7.0 a	*	17.4 ± 3.0 b	20.8 ± 1.1 a	ns
Control	24.0 ± 5.7 ab	25.3 ± 4.0 ab	ns	19.2 ± 3.5 ab	19.4 ± 1.5 a	ns

[z] All amendments were applied at the rate of 990 gm per 165 kg of Astatula fine sand. Data are means of three flats per treatment; seedling stand is the number germinating and growing of 50 seed planted; 10 plants per flat were measured on November 15, 1986.

[y] Mean ± standard error of colony-forming units (cfu) per gram of soil.

[x] Means in a column followed by the same small letter are not significantly different by Duncan': multiple range test (_P_ = 0.05).

[w] Probability that means in a row are significant at $\underline{P} < 0.05$ (*) or not significant (ns).

Table 6. *Fusarium* spp. and fluorescent pseudomonad colony-forming units (cfu) per gram soil in flats inoculated with *Fusarium solani*.

	Log ^{10} (cfu/g) mean ± se[z]					
	Fusarium spp.[y]			Fluorescent pseudomonads		
Amendment	Inoculated	Uninoculated		Inoculated	Uninoculated	
Humate	4.1 ± 0.2[y]b[x]	3.6 ± 0.1 a	ns[w]	0 b	0 b	ns[w]
Phosphoclay	3.3 ± 0.3 c	1.6 ± 1.4 b	ns	5.7 ± 0.2 a	5.3 ± 0.2 a	ns
Phosphogypsum	4.4 ± 0.1 ab	3.6 ± 0.6 a	*	5.8 ± 0.6 a	6.0 ± 0.2 a	*
Control	4.5 ± 0.2 a	3.6 ± 0.5 a	*	5.4 ± 0.6 a	3.4 ± 3.0 a	ns

[z] Mean ± standard error of colony-forming units (cfu) per gram of soil.

[y] Each flat was inoculated with a 300 ml aqueous suspension containing 6.7 x 106W spores of *Fusarium solani* per ml on August 19, 1986. Data are means of three flats per treatment taken on November 15, 1986.

[x] Means in a column followed by the same small letter are not significantly different by Duncan's multiple range test ($P < 0.05$).

[w] Probability that means in a row are significant at $P = 0.05$ (*) or not significant (ns).

Table 7. Sour orange growth, leaf, stem, and root symptoms and phytophthora-positive roots on plants grown in a greenhouse in two soils amended with phosphogypsum, phosphoclay, and humate.

Soil source and amendment ($kg \cdot ha^{-1}$)	Shoot dry wt (g)	Root dry wt (g)	Leaf sympt[z] (#/8)	Foot rot[y] (#/8)	Root rot[x] (0-5)	Phytophthora[w] (+) roots/plant
<u>Ft. Pierce</u>						
Control	43.3 a	13.3 a	6/8 a	2/8 a	3.0 a	3.5 ab
Phosphogypsum (17,621)	37.4 a	8.5 b	4/8 a	0/8 a	2.9 a	2.5 b
Phosphoclay (16,200)	30.5 b	6.8 b	6/8 a	2/8 a	4.4 a	3.8 a
Humate (16,200)	27.7 b	7.4 b	3/8 a	0/8 a	3.5 a	3.6 a
<u>Indiantown</u>						
Control	45.3 b	19.9 a	1/8 a	1/8 a	1.1 ab	2.4 a
Phosphogypsum (17,621)	49.7 b	20.1 a	1/8 a	0/8 a	0.3 b	0.9 b
Phosphoclay (16,200)	69.4 a	27.4 a	2/8 a	1/8 a	2.1 a	3.4 a
Humate (16,200)	50.0 b	18.5 a	3/8 a	1/8 a	2.8 a	3.6 a

[z] Leaf symptoms: interveinal chlorosis.

[Y] Stem symptoms: gumming at soil line.

[X] Root rot rating 0-5: 0 = no visible epidermal sloughing to 5 = extensive root rot.

[W] Four root pieces plated on PAPPH medium from each pot, eight pots per treatment. Test set up March 1987 and terminated November 1987. Means within columns and each soil type not sharing the same small letter are significantly different by Duncan's multiple range test at <u>P</u> = 0.05.

Table 8. Growth of *Phytophthora parasitica* on cornmeal agar (CMA) amended with phosphoclay and phosphogypsum.

Concentration of amendment in CMA (%)	Mean colony diam (cm)	
	Phosphoclay	Phosphogypsum
0.01	7.76 ns[z]	7.88 ns[z]
0.05	7.88 ns	7.94 ns
0.10	8.00 ns	7.96 ns
1.00	7.74 ns	6.58 **
Control	8.00	8.00

[z] Means of treatments compared with control (no amendment); double asterisk (**) = *P* = 0.01; ns = not significant.

Values are means of five 8-day-old colonies, one on each of five petri plates.

Figure 1. Sulfur in Oldsmar soil, April 1989 through August 1989, amended with three rates of phosphogypsum in March 1989

Figure 2. Calcium in Oldsmar soil, April 1989 through August 1989, amended with three rates of phosphogypsum in March 1989

FIG 1

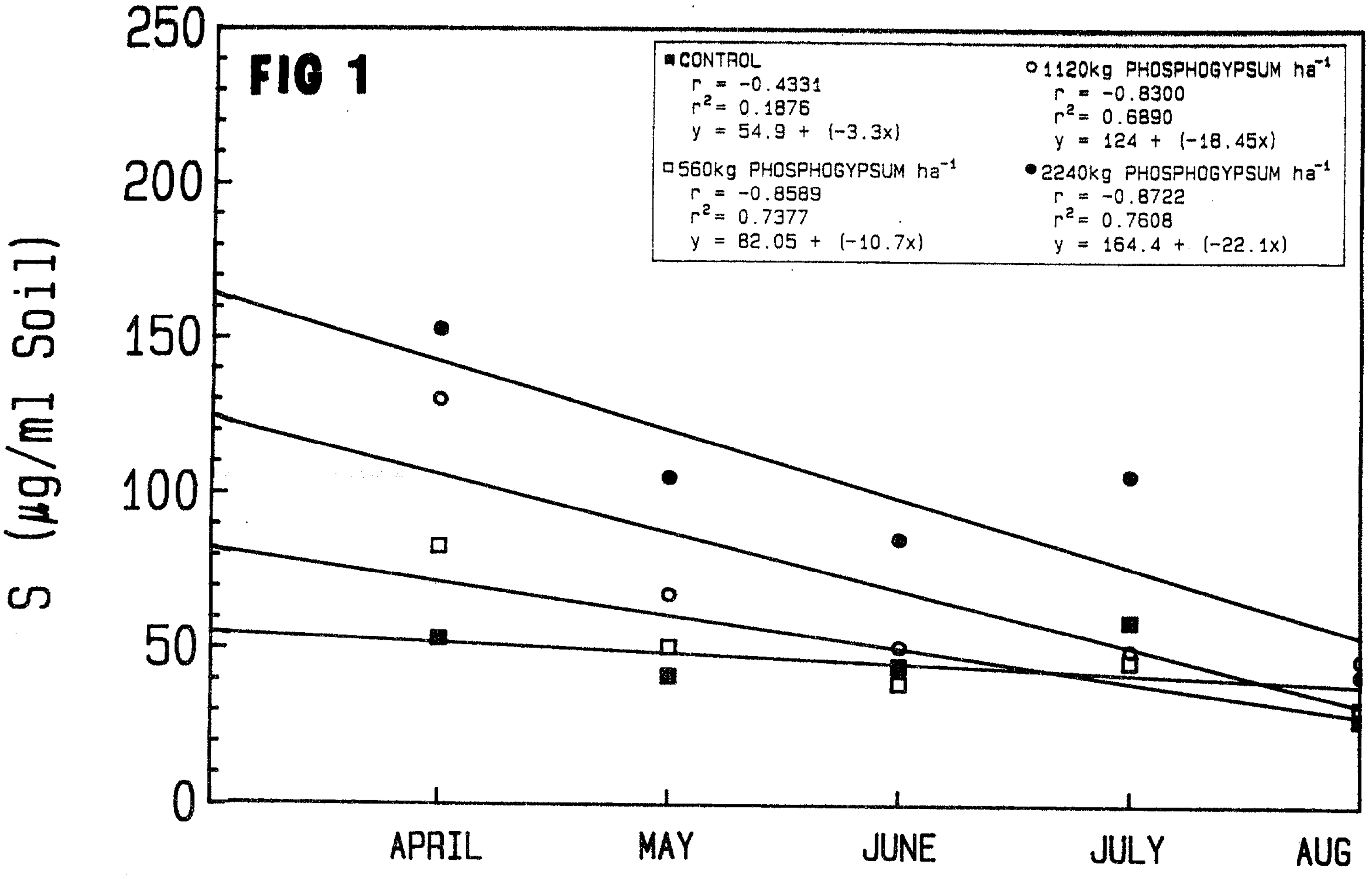
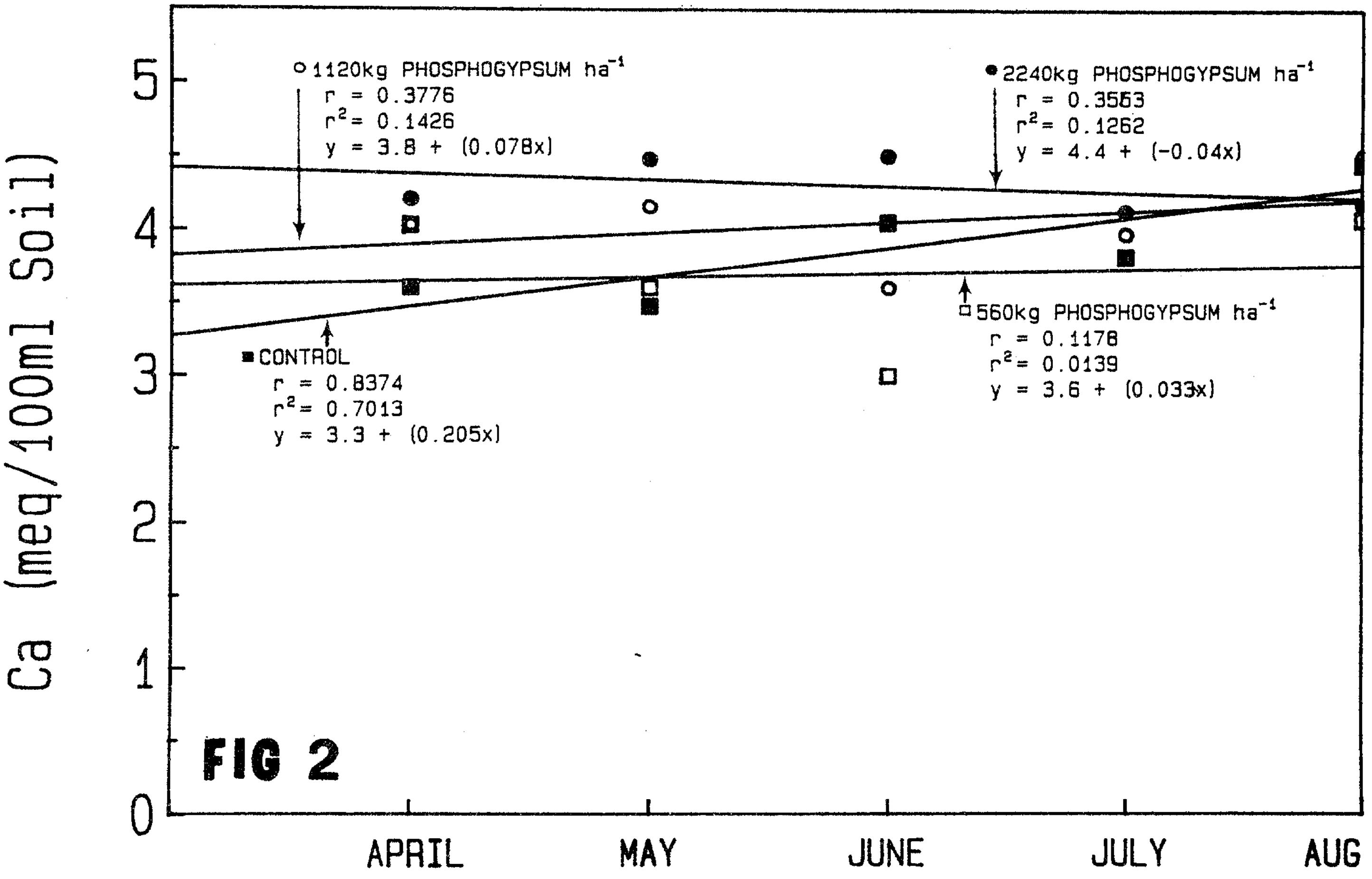


FIG 2



1989

AGRICULTURAL USES OF PHOSPHOGYPSUM ON CALCAREOUS SOILS

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ABSTRACT

The most important limiting factor nutrient in calcareous soil is phosphorus. The aim of this study was to investigate the effect of adding phosphogypsum (PG) and super phosphate fertilizer on calcareous soil on the growth and production of corn plant.

Corn zea mays. seeds were planted in a field experiment. Different rates of phosphogypsum were applied 0, 80, 160, 320, 640, and 1280 Kg PG/ha and two rates of super-phosphate fertilizer 80, and 160 Kgp/ha.

Corn plants were harvested and yield components were determined. Chemical analysis for plant and soil were determined too. Application of PG to the field positively affected the availability of

micronutrients. The concentrations of P, Fe, Zn, and Mn increased with increasing rates of PG application.

The results of plant analysis are in accord with the results of soil analysis.

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.

The most important limiting factor nutrient in calcareous soil is phosphorus. The availability of macro and micro nutrients are largely controlled by soil pH and to a lesser degree by organic matter, lime content, type of clay minerals, and climatical conditions. In arid and semi arid land contains considerable amount of lime with a pH of soil solution higher than 7.5, in these areas macro and micronutrients deficiencies have been reported. Chemosorption and precipitation of Fe, Zn and Mn by carbonate, were the main factors for controlling the solubility of these elements in soil.

To a certain degree the deficiency of micronutrient in calcareous soil can be corrected by application of acidifying materials.

The major acidifying materials used for soil acidification are: elemental sulphur, gypsum (mined or industrial), aluminum and iron sulphates. Since the application of acidifying materials to soil increase the solubility of micromutrient.

This experiment was conducted to study the effect of by-product phosphogypsum levels on the availability of P, Fe, Zn, and Mn in a calcareous soil and their content in corn.

MATERIALS AND METHODS

The experiment was conducted at Al-Rasheedia experimental station in Mosul city-north of Iraq. The climate in the area identified as arid to semi-arid. After land preparation, individual plots were divided 3m x 7m with one meter width as borders area between replicates.

The experiment laid out according to randomized complete block design with three replication per treatment. Before planting soil samples (0-30 cm) were taken from experimental unit to determine and measure some of chemical and physical properties (table 1). The procedures described by (Richard, 1954) were used for the determination of pH, Ec, CEC, lime, gypsum, and' texture. However organic matter were determined according to walkely-Black procedure as described by (Jackson, 1958). Extractable Fe, Zn, and Mn in soil were determined by the method described by (Soltanpour and

Table I. Some Physical and Chemical Characteristics of the Experimental Condition.

Soil test	Value.
Sand %	31.20
Silt %	32.60
Clay %	36.20
Texture	L
PH	7.60
Ec. ds/m.	1.10
O.M.%	1.65
CEC meq/100g.soil	26.20
Available P (ppm)	6.42
Available Fe (ppm)	10.80
Available Zn (ppm)	0.78
Available Mn (ppm)	12.60
Ca meq/L.	9.60
Mg meq/L.	1.50
$CaCO_3$ % tatal	24.20
$CaCO_3$ % active	7.90

Schwab, 1977). Phosphorus in soil was determined by (Olsen et al. 1954).

Corn Zea mays, was grown in July 16th 1989. Eight treatments of super phosphate and phosphogypsum were used in this study, they are as follows:-
80, and 160 Kg P/ha as super phosphate fertilizers,
6 and 80, 160, 320, 640, and 1280 Kg phosphogysum/ha.
Urea was added to all experiments units at the rate of 40 Kg N/ha. However potassium fertilizers was not added because it is believed the soil is capable to supply adequate potassium for corn crop. On November 2nd, corn plants were harvested, $2m^2$ per experimental unit were harvested for crop yield measurement. Corn seeds were ground in a stainless steel mill with 1mm sieve ring and analysed for P, Fe, Zn, and Mn by using the wet-digestion, this method was described by (Jackson, 1958).

Atomic absorption spectrophotameter unit was used for estimation of Fe, Zn, and Mn. However P was determined by using NH_4-Vanadate as described by (Richards 1954). Spectrophotometer unit was used for this determination.

Active lime was determined by using a solution of ammonium oxalate as described by (Yaalon, 1957).

RESULTS AND DISCUSSION

The results in table 1, revealed that the soil is alkaline in reaction not saline and contain appreciable amounts of calcium carbonate, beside that the soil is deficient in P and has low O.M. However the the result in table 2 indicated that Iraqi phosphogypsum (PG) is acidic in reaction.

Calcium sulphate in phosphogypsum is available as dihydrate $CaSO_4.2H_2O$, hemi- hydrate $CaSO_4.1/2H_2O$ and anhydrate $CaSO_4$, or it may also occur in combination of di-hydrate and hemi-hydrate, etc. depending upon the process involved in the production of phosphoric acid. The quality of phosphogypsum depends both on the process technology adapted as well as the quality of phosphate rock used. Atypical analyses of phosphogypsum was given in table 2. Phosphogypsum may also contain traces of iron, Zinc, and maganese. The presence of these elements is attributed to their presence in phosphate rock and impurities in sulphuric acid. Phosphogypsum is high-grade gypsum having purity more than 80% on air-dry basis as against 65-70% in agriculture grade mineral gypsum.

The physico-chemical effects of phosphogypsum an soils is similar to that of mineral gypsum. However, it is likely to be more effective and consequently economic because of the high percentage purity when

TableII: Chemical Compositions of Iraqi Phosphogypsum.

Component	Percent
CaO	32.94
SO_3	44.94
P_2O_5	0.18
F	0.60
SiO_2	0.45
Fe_2O_3	0.40
Al_2O_3	1.05
MgO	0.46
Crystal-H_2O	19.18
$CaCO_3$	4.29
pH	3.6
Gypsum	80.0
Ec	2.40 ds/m.

compared to agriculture grade mineral gypsum available for soil.

The yield component of corn after harvest as showed in table 3, revealed that plant height increased with increasing amounts of both super phosphate and phosphogypsum. Morever dry matter production was sharply increased with increasing additions of superphosphate. Highest dry matter production was found with higher level of super-phosphate 166 Kg P/ha. However, dry matter production also increased with different levels of phosphogypsum but into some extent less than with super phosphate additions, that may due to the effect of the purity of phosphogypsum beside the effect of sulphur and other elements. In addition of the percentage of P in phosphogypsum is very low compared that in commercial superphosphate fertilizer, but that may not load to exclude the beneficial of phosphogypsum for using it as amendment and/ or a nutritions product for agriculture particularly on calcareous soils.

It was also noticed that the numbers and weights of ters of corn were increased with increasing superphosphate and phosphogypsum amounts respectively as shown in table 3. Maximum weight of ters was given at 160 Kg P/ha as superphosphate. The data indicated that the concentrations of extractable P, Fe, Zn and Mn in general increased with increasing amounts of phosphogypsum as shown in table 4. Except that for Zn

Table III : Yield components of corn as affected by differents of super-phosphate and PG.

Material	Treatment Kg/ha	Plant hight (Cm)	Dry matter tan/ha	No. of ters/ha	Weight of ters ters/ha
Control	0.0	185	3.68	23350	5.4
Super-Phospate (P)	80	210	9.37	145.650	14.5
	160	232	12.87	155.000	17.6
Phospho-gypsum	80	190	3.82	155.000	6.2
	160	204	4.69	70.000	8.4
	320	215	5.82	95.000	9.5
	640	217	6.87	125.000	11.0
	1280	220	10.19	140.000	13.5

Table IV : Concentrations of extractable Fe, Zn, and Mn by DTPA -TEA in different treatments.

Material	Treatment Kg/ha	Concentration (ppm)			
		P mg/g	Fe ppm	Zn ppm	Mn ppm
Control	0.0	6.42	10.80	0.78	10.64
Super Phosphate as P	80	11.73	9.82	0.55	11.82
	160	16.92	8.41	0.41	11.13
Phosphogypsum	80	7.22	11.20	0.74	13.21
	160	8.45	12.32	0.69	13.75
	320	9.73	14.20	0.66	14.41
	640	10.52	16.41	0.61	15.63
	1280	12.54	18.24	0.57	16.21

the concentrations were decreased as the addition of phosphogypsum increased.

Rashid et al., (1989) concluded that the long lasting effect of phosphogypsum on the availability of micronutrient in soil is more likely related to the low solubility of this material. Meanwhile, the concentrations of extractable Fe, Zn and Mn decreased when superphosphate was added in both levels 80, and 160 Kg P/ha. This may due to the high purity of the superphosphate substance, and to the negative interactions that may happen between P with micronutrients in general.

The acidity nature of the 'by-product' phosphogypsum added to the soil may release some amount of the unavailable micro-nutrients either from soil or from phosphogypsum itself, but may need a considerable time. Some workers (Salih et al. 1987), (Haynes and Swift 1985), reported that the amounts of $CaCl_2$ -extractable Fe, Zn, and Mn were increased as the soil was acidified and they related such increases in solubility to dissolution of Fe-hydroxide, Mn-oxide and desorption of specifically adsorbed Zn. One year later (Haynes and Swift 1986), found that soil acidification increased the levels of extractable Fe, Mn and Zn when extracted by EDTA. Morever at low pH they found that Mn and Zn were relatively mobile in the soil, meanwhile Fe

Table V : Concentrations of P, Fe, Zn and Mn in Corn Seeds in Different treatments of SuperPhosphate and Phosphogypsum (PG).

Material	Treatment	Concentration			
	Kg/ha	P mg/g	Fe ppm	Zn ppm	Mn ppm
Control	0.0	4.26	92	60	72
Super Phosphate as P	80	7.85	88	57	67
	160	13.21	85	51	64
Phosphogypsum	80	4.36	96	66	78
	160	5.15	106	74	86
	320	5.83	115	82	97
	640	7.52	135	90	102
	1280	8.77	152	93	109

was not, which they related to the ability of Fe form a complex compound with soil organic matter.

Increasing the addition of phosphogypsum amount to the soil, the concentrations of P, Fe, Zn and Mn were increased in corn seeds as revealed in table 5. However, with addition of super-phosphate, the concentration of P was only increased in both rates 80 and 160 Kg P/ha.

Aclose results was found with the study done by (Rashid et al. 1989), However they used less amount of phosphogypsum than this study. Meanwhile (Mays et al. 1986) and have used a high rates of application. Applied a huge amounts of phosphogypsum to calcareous soil may cause areduction in pH but does not mean a sharp increase in micronutrients elements. Rashid et al. (1989) stated that applying acidified material on calcareous soil is buffered by base constituents mainly carbonates, the acidic property of phosphogypsum may be the reason for such large increase in the extractable Fe, Mn and Zn probably due to the localized decrease in soil pH as a result of phosphogypsum application. The localized decrease in soil pH may occured temporarily around the roots rhizosphere which may enhance the absorbtion of desorbed Fe, Mn and Zn by the surrounding contact root hairs. Morever phosphogypsum contains Fe, Mn and Zn as impurities.

Rashid et al. (1989) stated that the amount of trace elements absorbed by the plant were much greater than the phosphogypsum contents of these elements.

CONCLUSION

In this study it was found clearly that the effect of lime on reducing or percipitation Fe, Mn and Zn in soil may be decreased by acidifying the soil with phosphogypsum furthermore increasing the amounts of P in soil. However attention may be taken for other elements that have a negative effect on plant growth by the addition of phosphogypsum especially if added in a large amounts.

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"EFFECTS OF PHOSPHOGYPSUM AND POTASSIUM CHLORIDE ON THE NUTRICIONAL STATUS; PRODUCTION AND ORGANOLEPTICAL QUALITY OF PINEAPPLE FRUITS"

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ABSTRACT

Aiming to study the possibility to use potassium sulphate (K_2SO_4) instead of potassium chloride (KC1) plus phosphogypsum (PG) through plant nutritional status evaluation, pineapple production and fruit qualitative aspects, the presente work was carried out at Monte Alegre, county Minas Gerais State (MG) and Jaboticabal, county Sao Paulo (SP). The treatments were set by the use of two potassium sources, the sulphate (K_2SO_4) and the chloride (KCl), which were given at the dose of 12 g of K_2O/plant, following soil analysis recommendation. The potassium chloride was given in association with a set of increasing doses of phosphogypsum in amounts enough to give 0; 1/2; 1; 2 and 3 times the SO_4 level given in the treatment containing K_2SO_4.

The pineapple species used was *Ananas comosus* (L.) Merrill cv. Smooth Cayenne. The spacing used was 1.10 x 0.40 x 0.40m and 0.90 x 0.40 x 0.40m respectively considering the counties described above. It was used the casualized blocks for experimental desing, at Monte Alegre de Minas (MG) county 6 treatments were considered with 5 repetitions in Jaboticabal (SP) county in 6 treatments with 4 repetitions. According to the treatment characteristics, the freedom degrees were partitioned following the contrasts, $Y_1 = (T_1)$ vs $(T_2 + T_3 + T_4 + T_5 + T_6)$; $Y_2 = (T_2)$ vs $(T_3 + T_4 + T_5 + T_6)$; Y_3 = linear effect of phosphogypsum; Y_4 = quadratic effect of phosphogypsum and Y_5 = cubic effect of phosphogypsum. As for mean comparison, two at a time. A Tukey test was made at 5% of probability.

The treatment effect evaluation was carried out through leaves and fruit mineral analysis; soil chemical analysis and technological analysis such as: fruit mean weight with and without the crown; mean fruit size (height x diameter); pulp mean color; soluble solids percentage (Brix); total acidity and soluble solids/total acidity (ratio).

The results have shown that KCl has not had significative difference either associated with phosphogypsum or not on fruit production

(t/ha); K_2SO_4 has had stronger effects in relation to all treatments for the total acidity the soluble solids/total acidity (ratio) the levels of chlorine (Cl) were low in the treatments with K_2SO_4 followed by KCl + phosphogypsum and KCl alone the levels of S were low in the treatments with KCl alone, followed by KCl + phosphogypsum the different fruit parts, including the pulp, also at the experimental conditions it was not possible to obtain better or even similar results as those of K_2SO_4 through the association of KCl and phosphogypsum.

INTRODUCTION

The pineapplecrop is important among the food production. It is grown in all states of Brazil, which is the third in world production. Thailand and the Philipines being ahead of us. Our pineapple exports are little.

In Brazil, despite its importance, so far it did not have its due attention and research. As its cultivation is in acid soils and few nutrients, it was considered a plant of easy growth and little care. Though recent researches have shown a need for certain chemical elements, this plant responding very well to the use of these nutrients (Giacomelli et al, 1971; Lacoeuilhe & Gicquiaux, 1971; Melo et al., 1973; Ferraz et al., 1975). On the other hand, the incorrect use of nutrients or timing may bring about a great sharp decrease in production or the crop loss (Montenegro et al., 1967; Black & Page, 1970; Giacomelli, 1974).

Of all the most needed nutrients, the potassium uptake is the first, which increases production and quality, such as, better pulp characteristics with less acidity and better colouring outside. The potassium excess renders the pulp white, little consistent, more acid and with a longer stalk (Malavolta et al., 1967).

The potassium fertilizers most used are those which combined with chlorides and sulphates. Research has proven that potassium as sulphate yields heavier fruits, less acidity, and greater soluble solids percentage (Brix). Yet, due to prices and importation problems, it is practically absent in pineapple crops.

Therefore, this work envisages the possibility of substituting the potassium sulphate by potassium chloride associated with phosphogypsum. This will be measured through production and quality.

MATERIALS AND METHODS

The research was carried out in two different places once in Minas Gerais (MG) State, the other in Sao Paulo (SP) State, both in dark red Latosol (Oxisol), the main chemical characteristics being as shown in Table I.

TABLE I. The soil sample characteristics (Methodology as described by Raij & Quaggio, 1983, except the sulphur, according to Vitti (1989).

pH $CaCl_2$	M.O. (%)	P	$S-SO_4$	K	Ca	Mg	H+Al	S	T	V (%)
		ug/cm^3		-----------	meq/100 cm^3	-------------				
					Minas Geraís (MG)					
4.2	2.7	6	3	0.04	0.08	0.20	3.40	1.0	4.4	23
					São Paulo (SP)					
5.0	2.3	32	1	0.22	1.80	0.90	3.10	2.92	6.0	49

The specie used was the *Ananas comosus* (L.) Merrill, cv. Smooth Cayenne. The shoots stalk slip, weighing about 400g each, were previously treated against diseases. The planting was made in march 17.87 and April 15.87 respectively in Minas Gerais (MG) and Sao Paulo States. The spacing was 1.10 x 0.40 x 0.40m and 0.90 x 0.40 x 0.40m with approximate population 33,000 and 41,500 plants per ha respectively for MG and SP works. In Minas Gerais the liming was 2,000 kg per ha, with dolomitic limestone in order to increase the saturation in the base to about 50%.

The basic fertilization in the furrow was 3.0 Minas Gerais(MG) and 2.0g P_2O_5 per plant in Sao Paulo (SP) as triple superphosphate (TSP, 42% P_2O_5). In the top-dressing the fertilization was distributed as close as possible to the plants, following this order: two months after planting were applied 3g N per plant as urea (45% N) seven months after planting 6g N per plant as urea, plus 3.0 in Minas Gerais (MG) and 2.0g P_2O_5 per plant as TSP in Sao Paulo (SP); eight and eleven months after planting were applied 9.0g N per plant as urea. In April 88 the blooming was induced using a Ethrel and 2% urea with the dosage of 50 ml per plant.

The potassium sources were two: the chloride (KCl) and the potassium sulphate (K_2SO_4), the dosage used was 12g of K_2O per plant, based on the recommendation of soil analysis. The KC1 was applied in growing amounts of phosphogypsum, in the proportions necessary to supply 0, 1/2, once, twice and three the sulphate amount in the K_2SO_4 treatment (Table II).

The potassium and phosphogypsum application was done on the top-dressing divided in three times: first time in 2 months, second time is 7 months, and the third in 12 months after planting. Casualized blocks were used in the experimental design: 6-treatments in Minas Gerais (MG) with 5 repetitions and 4 repetitions in Sao Paulo (SP).

TABLE II. Sources and dosages of K_20 as treatments associated or not to phosphogypsum usage.

Treatments	K_2O sources	g/planta nutrient				Fertilizer sources amounts	
		K_2O	Ca	Cl	SO_4	potassium	phosphogypsum
T_1	K_2SO_4	12.0	-	-	12,0	24.0	-
T_2	KCl	12.0	-	9.0	-	20.0	-
T_3	KCl+PG	12.0	2.38	9.0	6.0	20.0	12.5
T_4	KCl+PG	12.0	4.76	9.0	12.0	20.0	25.0
T_5	KCl+PG	12.0	9.52	9.0	24.0	20.0	50.0
T_6	KCl+PG	12.0	14.28	9.0	36.0	20.0	75.0

Note: K_2SO_4 (50% K_2O and 17% S)
KCl (60% K_2O and 47% Cl)
PG (phosphogypsum 16% S)

According to the treatment characteristics, the freedom degrees were partitioned following the contrasts;

Y_1 is a comparison between T_2 and all the other treatments that is (T_1) vs $(T_2 + T_3 + T_4 + T_5 + T_6)$;
Y_2 is a comparison between T_2 and all the other treatments with phosphogypsym tha is (T_2) vs $(T_3 + T_4 + T_5 + T_6)$;
Y_3 = linear effect of phosphogypsum dosage;
Y_4 = quadratic effect of phosphogypsum dosage;
Y_5 = cubic effect of phosphogypsum dosage.

For comparing the average two at a time the Tukey test was carried out at the 5% level of probability.

The experimental plots were 4 double lines, each line having 40 plants (20 plants per line). From the 160 plants as a whole, the 60 from the middle were used as sampling.

As the spacings of the two counties were different:

. Minas Gerais (MG), 48.00 m^2 in the whole, being 19.20 m^2 of used area;
. Sao Paulo (SP), 31.20 m^2 in the whole, being 12.48 m^2 of used area.

The leave sampling was carried out 9 and 10 months after planting 15 "D" leaves were collected per plot for macronutrients and chlorine analysis.

The harvest was in January 89. From a sampling of 20 fruits per plot, the following assessmentswere made: fruit weight, with and without the crown, average size of the fruit (height and diameter), pulp colour, soluble solids (Brix) using a rephratometer (A.O.A.C., 1965) as well as total acidity (Giacomelli, 1982).

RESULTS AND DISCUSSION

RESULTS

Fruit Physical and Chemical Characteristics and Production

The results of the physical and chemical production and characteristics on the pineapple and the statistical analysis summary are in Tables III and IV. Though the average fruit weight did not show statistically meaningful differences comparing the treatments, these guidelines presented a wide range of variations in the results mainly the Sao Paulo treatments. So, the T_5 treatments (KCl + 2PG level) and T_6 (KCl + 3PG level) yielded an average fruit weight, with and without crown, larger comparing to the other treatments, Yielding greater expected weights of about 2 to 3 t/ha of fruits in Minas Gerais (Table III). In Sao Paulo, the treatments T_l (K_2SO_4), T_4 (KCl + 1PG level), T_5 (KCl + 2PG level) and T_6 (KCl + 3PG level) yielded greater average weight compairing to the T_2 (KCl and no PG) treatment, yielding more 3 to 9 t/ha.

Comparing only the potassium sources, the T_1 and T_2 treatments, the results are no differences in the average fruit weight. These results disagree with several researchers who presented better K_2SO_4 results. These are Samuels & Gandia Diaz (1960); Su & Li (1962); Beaton (1966) and Lacoeuilhe (1978) and according to the results of Chadha et al. (1975); Subramanian et al. (1977), Bezerra et al. (1983) and Reinhardt & Neiva (1986).

In the Sao Paulo work, the average fruit size a meaningful difference in the fruit weight in the Y_l contrast, showing the K_2SO_4 advantage over the other treatments according to the results of Su & Li (1962). The same meaningful and positive result was shown in the average pulp colouring to this contrast (Y_1), showing again the K_2SO_4 advantage. As for the soluble solids percentage (Brix) there were no meaningful differences according the Bezerra et al. (1973); Chadha et al. (1975) and Subramanian et al. (1977) results.

Considering the total acidity the two works show that the T_1 (K_2SO_4) treatment presented the lowest total acidity, while the T_2 (KC1 and no PG) presented the highest total acidity, showing this way that the K_2SO_4 was more advantageous than the chloride, according to the Su & Li (1962) and Zehler et al. (1986) date. The ratio presented a similar result as for the total acidity. The highest were the T_1 (K_2SO_4)treatment and the lowest were the T_2(KCl and no PG) treatment in the two works.

The Tables V and VI present the macronutrients and chlorine levels in the fruits in its different part (shell, pulp, central axis). There

TABLE III. Average for production of the physical and chemical characteristics of pineapple and statistical analysis summary (average five repetitions), Minas Gerais (MG).

	Fruit weight with crown (g)	Yield t/ha	Fruit weight without crown (g)	Yield t/ha	Fruit height (cm)	Fruit diameter (cm)	Stalk diameter (cm)	Pulp colouring	Soluble solids (ºBrix)	Total acidity	Ratio
Averages T_1	1510.40	49.84	1349.60	44.53	15.93	11.68	2.76	4.26	15.8	0.51	30.37
T_2	1519.27	50.13	1356.73	44.77	15.50	12.04	2.67	4.40	15.2	0.68	22.55
T_3	1551.40	51.16	1387.20	45.76	15.53	12.04	2.68	4.11	14.8	0.65	23.19
T_4	1478.73	48.79	1336.53	44.10	15.81	11.56	2.81	4.18	16.3	0.62	26.35
T_5	1600.80	52.82	1449.47	47.83	15.96	11.59	2.78	4.32	16.3	0.63	25.89
T_6	1559.97	51.46	1403.17	46.30	16.13	12.11	2.82	4.29	16.0	0.65	24.84
Statistical d.m.s. (Tukey 5%)	-	-	-	-	-	-	-	-	-	0.13	7.11
F for blocks	0.48ns	0.47ns	0.44ns	0.44ns	1.87ns	1.31ns	0.72ns	0.12ns	0.63ns	0.08ns	0.13ns
F for treatments	0.40ns	0.40ns	0.36ns	0.36ns	0.40ns	0.85ns	0.90ns	0.30ns	2.17ns	4.10*	3.06*
Y_1	-	-	-	-	-	-	-	-	-	18.13	11.01**
Y_2	-	-	-	-	-	-	-	-	-	2.83ns	1.01ns
Y_3	-	-	-	-	-	-	-	-	-	1.70ns	1.99ns
Y_4	-	-	-	-	-	-	-	-	-	0.41ns	1.50ns
Y_5	-	-	-	-	-	-	-	-	-	0.23ns	0.63ns
CV (%)	9.85	9.90	11.34	11.35	5.63	5.22	5.50	9.93	5.87	10.56	13.99

Y_1 = T_1 vs ($T_2 + T_3 + T_4 + T_5 + T_6$); Y_2 = T_2 vs ($T_3 + T_4 + T_5 + T_6$); Y_3 - linear effect of PG; Y_4 - quadratic effect of PG;
Y_5 = cubic effect of PG; ns - no meaningful; * e ** meaningful respectively for level 5 and 1%.

TABLE IV. Average for production of the physical and chemical characteristics of pineapple and statistical analysis summary (average four repetitions), São Paulo (SP).

	Fruit weight with crown (g)	Yield (ha)	Fruit weight without crown (g)	Yield (ha)	Fruit height (cm)	Fruit diameter (cm)	Stalk diameter (cm)	Pulp colouring	Soluble solids (ºBrix)	Total acidity	Ratio
Averages T_1	1445.36	59.98	1245.71	51.70	15.38	12.15	2.55	4.45	14.42	0.63	23.13
T_2	1191.05	49.43	1006.09	41.75	13.94	11.23	2.37	3.87	13.75	0.81	17.08
T_3	1220.24	50.64	1038.15	43.08	14.40	11.73	2.46	4.05	14.05	0.76	18.57
T_4	1398.63	58.04	1160.89	48.18	14.44	12.10	2.45	3.64	13.70	0.73	18.80
T_5	1278.51	53.06	1088.10	45.16	14.52	11.84	2.32	3.76	14.55	0.64	17.53
T_6	1319.27	54.75	1085.88	45.06	14.41	11.23	2.40	3.62	14.02	0.82	17.34
Estatistical											
d.m.s. (Tukey 5%)	-	-	-	-	1.17	-	-	0.71	-	0.10	4.74
F for blocks	4.81*	4.24*	4.10*	4.08*	4.22*	0.45ns	6.10**	3.79*	1.70ns	1.17ns	0.99ns
F for treatments	2.85ns	2.67ns	2.60ns	2.58ns	3.41*	2.77ns	0.95ns	4.14*	1.03ns	4.98**	4.79**
Y_1	-	-	-	-	13.79**	-	-	15.35**	-	18.31**	21.58**
Y_2	-	-	-	-	3.13ns	-	-	0.38ns	-	0.33ns	0.76ns
Y_3	-	-	-	-	0.01ns	-	-	2.16ns	-	3.77ns	1.81ns
Y_4	-	-	-	-	0.12ns	-	-	0.55ns	-	0.10ns	0.00ns
Y_5	-	-	-	-	0.01ns	-	-	2.24ns	-	2.39ns	0.31ns
CV (%)	9.01	9.18	9.78	9.78	3.51	4.18	6.89	7.89	4.84	8.94	11.00

$Y_1 = T_1$ vs $(T_2 + T_3 + T_4 + T_5 + T_6)$; $Y_2 = T_2$ vs $(T_3 + T_4 + T_5 + T_6)$; Y_3 - linear effect of PG; Y_4 - Quadratic effect of PG; Y_5 = cubic effect of PG; ns = no meaningful; * e ** - meaningful respectively for level 5 and 1%.

TABLE V. Average nutrients amounts (%) in the pineapple fruit and statistical analysis summary (average five repetitions), Minas Gerais (MG).

	SHELL						PULP						CENTRAL AXIS					
	P	S	Cl	K	Ca	Mg	P	S	Cl	K	Ca	Mg	P	S	Cl	K	Ca	Mg
Averages T_1	0,09	0,08	0.16	1,07	0,34	0,10	0.08	0.05	0,07	1,09	0.29	0.12	0,02	0.011	0,06	0,68	0.25	0.13
T_2	0,09	0,05	0,60	1.19	0,29	0.08	0.07	0.03	0.23	1.02	0.27	0,11	0.02	0.005	0.24	0.81	0.23	0,09
T_3	0,09	0.08	0,53	1.15	0,26	0.08	0,07	0.05	0.17	0,97	0.24	0.08	0.03	0.011	0.17	0,72	0.23	0.08
T_4	0.09	0.08	0.45	1.11	0.28	0.08	0,07	0.05	0.19	0.95	0.25	0.09	0,02	0.012	0.18	0,72	0.25	0.10
T_5	0.08	0,07	0.40	1.05	0,32	0.08	0.07	0.05	0.13	0.95	0.25	0.08	0.02	0.013	0.17	0.65	0.20	0.11
T_6	0.08	0,08	0.53	1.14	0,28	0,08	0.07	0.05	0.16	0,97	0,26	0.09	0.02	0.012	0.17	0.70	0,11	0.11
Statistical																		
d.m.s. (Tukey 5%)	-	0,01	0.14	0.12	0.06	0.02	-	0.01	0,05	0.09	-	0.03	-	0,005	0,04	0.12	0,06	0,04
F for blocks	1.10ns	0.28ns	0,33ns	0.73ns	1.02ns	0.88ns	1.16ns	0,84ns	1.59ns	0.55ns	2.39ns	1,01ns	0.65ns	0.27ns	0.22ns	2.39ns	0.74ns	1.49ns
F for treatments	1.75ns	15.24**	25,38**	3,67*	4,26**	2.74*	0.43ns	11.92**	22.71**	6.94**	2.25ns	5.57**	0.70ns	9.03**	43,41**	3,76*	14.12**	4.36*
Y_1	-	2,55ns	100,43**	3.95ns	10,33**	11.17**	-	1.33ns	70,43**	26,04**	-	14.53**	-	0.10ns	165.49**	1,56ns	7,91*	14.49**
Y_2	-	70,05**	13,19**	6.17*	0.04ns	1.21ns	-	53.89**	26,83**	7.92*	-	10.00**	-	43.40**	51,09**	12,78**	2,97ns	1,69ns
Y_3	-	2,05ns	0.00ns	0,19ns	2.74ns	0,07ns	-	0.09ns	4.38*	0.05ns	-	0.69ns	-	0.16ns	0.01ns	0.83ns	48.15**	4.08ns
Y_4	-	1.22ns	13.24**	7,61*	7,61*	0.96ns	-	3.87ns	4.16ns	0,59ns	-	1.91ns	-	0.03ns	0,09ns	2,19ns	10,66**	1.37ns
Y_5	-	0,36ns	0,04ns	0.44ns	0,60ns	0.31ns	-	0.44ns	7.79*	0.09ns	-	0,68ns	-	1.45ns	0,36ns	1,45ns	0,90ns	0.19ns
CV (%)	8.46	10,12	15.52	5.36	10,81	12.17	11.19	11.62	15.83	4,55	10,07	13,93	16.50	21.03	11,94	8.30	15.11	17,85

Y_1 = T_1 vs (T_2 + T_3 + T_4 + T_5 + T_6); Y_2 = T_2 vs (T_3 + T_4 + T_5 + T_6); Y_3 - linear effect of PG; Y_4 - quadratic effect of PG; Y_5 - cubic effect of PG
[illegible]ful; * e ** meaningful respectively for level 5 and 1%.

TABLE VI. Average nutrients amounts (%) in the pineapple fruit and statistical analysis summary (average four repetitions), São Paulo (SP).

	SHELL						PULP						CENTRAL AXIS					
	P	S	Cl	K	Ca	Mg	P	S	Cl	K	Ca	Mg	P	S	Cl	K	Ca	Mg
Averages T_1	0.08	0.06	0,10	1.21	0,29	0.09	0,08	0,05	0,09	1,24	0,24	0.10	0,02	0,019	0.13	1.28	0,20	0.05
T_2	0.08	0.04	0.66	1.44	0.28	0.07	0.08	0,03	0.33	1.23	0,28	0.09	0.03	0,005	0.30	1,34	0.28	0,08
T_3	0.07	0,06	0,61	1,39	1,39	0.07	0.07	0.07	0,05	1.29	0.23	0,09	0,03	0,013	0.21	1.31	0.26	0.07
T_4	0.08	0,06	0,58	1,44	0,33	0,08	0.06	0,05	0.10	1.14	0.22	0.08	0,03	0.018	0.26	1.46	0.25	0,08
T_5	0,08	0,06	0,68	1,46	0.35	0.08	0.05	0.05	0.18	1,14	0.35	0.07	0.03	0,016	0,29	1,15	0.25	0.07
T_6	0,07	0,06	0.58	1.43	0.34	0.07	0,06	0.05	0.20	1.12	0.33	0,07	0.03	0.018	0.27	1.33	0.29	0.08
Statiscical																		
d.m.s. (Tukey 5%)	-	0.01	0.11	0.19	-	-	0,02	0.01	0.07	-	0,06	0,03	-	0,006	0.11	0,21	0.06	-
F for blocks	2,16ns	0,40ns	1,31ns	0,57ns	0.28ns	0.83ns	1.22ns	1,15ns	1,39ns	1,45*	3,95*	1.14ns	2.52ns	0.64ns	3.68*	2.20ns	6.55**	1.49ns
F for treatments	1,29ns	11.02**	77.13**	4.89**	2.02ns	2,63ns	4.14*	5,64*	29.60**	2,46ns	21,59**	3,70*	1,08ns	15.36**	7,34**	4,81**	5.62**	0.69ns
Y_1	-	0.09ns	372.47**	22.90**	-	-	5.06*	0.69ns	31.94**	-	9.84**	10.49	-	13,75**	28.75**	0.57ns	21.94**	-
Y_2	-	54,83**	2.85ns	0.02ns	-	-	6.95*	27,25**	95,15**	-	0.05ns	2.03	-	55,23**	1.96ns	0.21ns	0.19ns	-
Y_3	-	0,01ns	0.03ns	0.39ns	-	-	3,61ns	0.01ns	9.04**	-	69,80**	3.82ns	-	2.67ns	3.35ns	2.01ns	0.84ns	-
Y_4	-	0.15ns	4.69*	1.12ns	-	-	2,59ns	0.00ns	3.38ns	-	8.04*	1.66ns	-	0.68ns	2.50ns	2.74ns	0.78ns	-
Y_5	-	0.01ns	5.62*	0.01ns	-	-	1.69ns	0.27ns	8,52*	-	20.23**	0.32ns	-	4.49*	0.12ns	18.64**	4.37ns	-
CV (%)	10.58	7.93	9,28	6.02	12,13	10.26	9.69	13.30	18.03	7,39	9.00	13,53	13.83	18,46	19,72	7.12	10.69	14.66

$Y_1 = T_1$ vs $(T_2 + T_3 + T_4 + T_5 + T_6)$; $Y_2 = T_2$ vs $(T_3 + T_4 + T_5 + T_6)$; Y_3 - linear effect of PG; Y_4 - quadratic effect of PG; Y_5 - cubic effect of PG
ns - no meaningful; * e ** - meaning respectively for level 5 and 1%.

data show a great difference in the amounts of sulphur and chlorine presenting the following decreasing order for the sulphur amount: K_2SO_4, KCl+PG and KCl. There was less sulphur in the central axis, while in shell and pulp they were both higher. The chlorine amounts though presented for greater percentages in the shell. The stalk and pulp presented both lower chloruro amounts.

Leaf Analysis

The Tables VII and VIII present the macronutrient amounts their relationship and chlorine amount in the "D" pineapple leaf (no chlorophil part) which used more nutrient amounts comparing to the chlorophiled part in samplings carried out 9 months after planting.

The KCl without phosphogypsum (KCl and no PG) presented less sulphur amounts in the leaves, while K_2SO_4 and KCl plus PG presented higher amounts and equal for both the K_2SO_4 and KCl plus PG treatment. This can be seen in the meaningful contrast Y_2.

The chlorine amounts in the-leaves were lower in the K_2SO_4 treatments. This can be seen in the meaningful Y_1 contrast.

DISCUSSION

Inspite of no meaningful differences favouring the KC1 plus PG mixture, mainly in the technological characteristic differences like in total acidity and ratio, the chlorine amount in various parts of the plant and especially in the fruit pulp, the chlorine amounts were less. On the other hand higher sulphur amounts indicating the possibility of lower chlorine uptake. Further studies are necessary for more conclusive data because several factor like: rainfall, application techniques dosage as well may have limited the positive effect of the KC1 plus phosphogypsum (KC1 plus PG) in the higher quality as envisaged.

CONCLUSION

This work presents the following results:

1. There was no meaningful differences between potassium sources and potassium chloride (KCl) plus phosphogypsum (PG) in the fruit yield;

2. The potassium sulphate (K_2SO_4) showed to be better than potassium chloride (KCl) in fruit quality in that is showing less total acidity and higher ratio;

3. The chlorine amounts in the potassium sulphate (K_2SO_4) treatments were lower in various parts of the plants, the potassium chloride plus phosphogypsum (KCl plus PG) presented intermediate chlorine amounts, and the KCl and no phosphogypsum (KCl and no PG)treatment

TABLE VII. Average amounts (X) and relationships nutrients in the "D" leaf of pineapple and statistical analysis summary (average five repetitions), Minas Gerais (MG).

	N	P	K	Ca	Mg	S	Cl	N/P	N/K	N/S	P/S	K/Ca	K/Mg	Ca/Mg	K/Ca+Mg	S/Cl
Averages T_1	2.32	0.29	5,24	0,38	0.46	0,15	0,19	8,08	0,44	15,06	1.87	13,82	11.45	0,83	6,25	0,89
T_2	2,01	0.27	5,45	0,29	0,23	0,12	1,01	7,33	0,40	16,79	2,33	19.21	23.64	1,24	10.59	0.12
T_3	1,98	0,28	5.33	0,35	0.27	0.16	0.94	7.08	0,37	12,48	1.77	15,29	19,64	1,29	8,35	0,17
T_4	2,13	0,27	5,19	0.34	0.28	0.15	0.87	7.89	0,41	13,82	1.76	15.59	18,61	1.94	8,48	0,18
T_5	2,19	0.25	5.17	0,39	0,31	0.18	0.95	8,66	0,42	12,35	1.44	13,66	16.84	1,26	7.50	0.19
T_6	1,94	0.26	4,45	0.51	0.28	0.16	1.08	7,40	0,44	12.13	1,66	8.94	16,42	1.89	5.71	0.15
Statistical																
d.m.s. (Tukey 5%)	0,29	-	0,76	0.09	0.08	0.02	0,19	-	0.07	2.05	0.31	3.63	4,32	0.42	1.86	0,28
F for blocks	1,76ns	0.73ns	2.07ns	1,52ns	1.90ns	1.67ns	3,42*	0.29ns	2.11ns	1.94ns	1.75ns	1.58ns	1,91ns	1.13ns	1.90ns	1.00ns
F for treatments	5.09**	1.35ns	4,22**	13,94**	19.12**	12.33**	58.49**	2.33ns	3,00*	16.15**	18.05**	16,85**	17.27**	13.26**	17.00**	22.92**
Y_1	14,77**	-	0,42ns	0.09ns	86.83**	0.01ns	278.23**	-	4.03ns	9.33**	0.93ns	0.62ns	50.86**	28.17**	16.72**	113,91**
Y_2	0.57ns	-	4,56*	24.65**	7.10*	50.86**	1.25ns	-	0.16ns	63.24**	74.75**	41,26**	28,18**	2,69ns	43.41**	0,47ns
Y_3	0.28ns	-	12.94**	37.92**	0.02ns	0,95ns	8.74**	-	9.00**	2.36ns	4.15ns	37,27**	6,76*	23.04**	25,17**	0.07ns
Y_4	9,95**	-	2,31ns	7.01*	1.58ns	3,96ns	3.65ns	-	1.04ns	0,96ns	6.55*	5,15*	0,51ns	12.30**	2.63ns	0.13ns
Y_5	0.00ns	-	0,90ns	0,05ns	0,35ns	1,67ns	0,58ns	-	0.76ns	4,88*	3.85ns	0.03ns	0.02ns	0,13ns	0,10ns	0,02ns
CV (%)	6.90	8.61	7,48	11.77	13.34	7,87	11.37	11.05	8,11	7,48	8.69	12.67	12,21	16.36	11.07	49.14

$Y_1 = T_1$ vs $(T_2 + T_3 + T_4 + T_5 + T_6)$; $Y_2 = T_2$ vs $(T_3 + T_4 + T_5 + T_6)$; Y_3 - linear effect of PG; Y_4 - quadratic effect of PG; Y_5 - cubic effect of PG; ns - no meaningful; * e ** - meaningful respectively for level 5 and 1%.

TABLE VIII. Average amounts(X) and relationships nutrients in the "D" leaf of pineapple and statistical analysis summary (average four repetitions), Sao Paulo (SP).

	N	P	K	Ca	Mg	S	Cl	N/P	N/K	N/S	P/S	K/Ca	K/Mg	Ca/Mg	K/Ca+Mg	S/Cl
Averages T_1	1.55	0.22	5,02	0,26	0.28	0.19	0.34	7.77	0.31	8,02	1,12	19,21	17.85	0.93	9.25	0,59
T_2	1,36	0.23	4,19	0.26	0.20	0.13	1.43	5.85	0.32	10.83	1,85	16,39	20,89	1.28	9.61	0.09
T_3	1,44	0.23	4,69	0.27	0.21	0.18	1.50	6.29	0.31	8,02	1.29	17.88	22.78	1.28	10.03	0,12
T_4	1,47	0.21	4.68	0,27	0,19	0.17	1.58	7,01	0.31	8,53	1.24	17.67	24.00	1.37	10.75	0.11
T_5	1.53	0.21	4.75	0.49	0.19	0.18	1.65	7,30	0,32	8.53	1,17	9,85	25.41	2.62	7.07	0.11
T_6	1.43	0.21	4.38	0.49	0.19	0.19	1,70	7,01	0,33	7,43	1.07	9.03	24.88	2.76	6.25	0.11
Statistical																
d.m.s. (Tukey 5%)	-	-	-	0.08	0.05	0.02	0.31	1.76	-	1,84	0,30	3,59	4.44	0.40	2.18	0,17
F for blocks	3.94*	0.40ns	0.29ns	5.67**	1,83ns	10.29**	0,92ns	2,42ns	5.04*	0,88ns	4.75*	2,86ns	1.47ns	1.60ns	2.71ns	1,04ns
F for treatments	1.32ns	1,44ns	2.05ns	42,97**	10,14**	21.55**	56.79**	3,29*	0,75ns	8.73*	18.77**	31,85**	8,71*	81,48**	12.32**	27,33**
Y_1	-	-	-	21,83**	46.64**	14.98**	273.23**	6,63*	-	2,16ns	7,78*	34,79**	29,51**	97,03**	0.69ns	136,29**
Y_2	-	-	-	36.42**	0.65ns	85.18**	5,72*	6,04*	-	36,32**	79,50**	10,15**	9,77**	57.14**	3,49ns	0,50ns
Y_3	-	-	-	130.49**	3.25ns	4,89*	4,77*	1.55ns	-	1,49ns	6.53*	100,55**	2,83ns	224,87**	46,96**	0,01ns
Y_4	-	-	-	7.56*	0.07ns	2.42ns	0,20ns	2,10ns	-	3,68ns	0,00ns	3,22ns	1,42ns	8.56*	0,22ns	0,06ns
Y_5	-	-	-	18,58**	0.11ns	0,30ns	0,03ns	0.13ns	-	0,01ns	0.05ns	10,55**	0,01ns	19.83**	10,22**	0,00ns
CV (%)	8.37	8.65	8.88	10.56	11.33	6,13	9,93	11.15	6,33	9,37	10,22	10.41	8.53	10,11	10,67	40,13

Y_1 = T_1 vs (T_2 + T_3 + T_4 + T_5 + T_6); Y_2 = T_2 vs (T_3 + T_4 + T_5 + T_6); Y_3 - linear effect of PG; Y_4 - quadratic effect of PG; Y_5 - cubic effect of PG; ns - no meaningful; * e ** - meaningful respectively for level 5 and 1%.

presented higher amounts. As for the sulphur amounts, this was the decreasing order: K_2SO_4 greater than KCl plus PG ad KCl and no PG;

4. In these conditions it was not possible to verity the potassium chloride plus phosphogypsum mixture substituting the potassium sulphate.

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Wheat Forage Response to Tillage and Sulfur Applied as Phosphogypsum

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ABSTRACT

Soil compaction and S deficiencies can be limiting factors in wheat (Triticum aestivum L.) production on Coastal Plain soils of the southeastern United States. Low S can also decrease forage quality. Field studies were conducted for three years to evaluate winter wheat forage response to annual applications of S applied as phosphogypsum under two tillage systems. The studies were conducted on a Benndale fine sandy loam (coarse-loamy, siliceous, thermic, Typic Paleudults) and a Dothan fine sandy loam (fine-loamy, siliceous, thermic, Plinthic Paleudults). Treatments included two tillage methods (turn-disk and disk only), two N rates (134 and 202 kg ha^{-1}), five rates of S (0, 11, 22, 45, and 90 kg ha^{-1}) and two times of S application (fall and spring). Total forage yields were affected by tillage during all three years of the study on the Dothan soil. On the Benndale soil a response to tillage was observed during the third year of the study. The conventional tillage system (turn-disk) consistently produced the highest yields. Forage yields on both soils were increased by the application of N and S. Yield responses to fall versus spring applied S were inconsistent and varied between locations. Tillage effects were not eliminated by applying higher rates of N and S. Results of this study show that phosphogypsum is an effective source of S on sandy Coastal Plain soils. The rates of

phosphogypsum applied in this study had little effect on the level of Ra-226 in the treated soil or harvested forage.

INTRODUCTION

Soil compaction and S deficiencies can be limiting factors in wheat (_Triticum aestivum_ L.) production on Coastal Plain soils of the southeastern United States. Coastal Plain soils have a low adsorption capacity for S and typically have low levels of extractable sulfate-S (Mitchell and Blue, 1981; Neller, 1959; Rabufetti and Kamprath, 1977; Reneau and Hawkins, 1980; Rhue and Kamprath, 1973). Many Coastal Plain soils are susceptible to compaction and the development of tillage pans is common. In the southeastern United States deep tillage is usually necessary to optimize wheat yields (Hargrove and Hardcastle, 1984; Karlen and Gooden, 1987; Touchton et al., 1989; Touchton and Johnson, 1982). Sulfur deficiencies on wheat are likely to occur in soils that have a sandy surface layer and a tillage pan that restricts root growth into the subsoil (Oates and Kamprath, 1985).

Forage and row crops have been shown to respond to applied S in the southeastern United States (Jordan, 1964; Rabuffetti and Kamprath, 1977; Reneau and Hawkins, 1980; Jones et al., 1982; Mitchell and Blue, 1989; Oates and Kamprath, 1985; Thompson and Neller, 1963; Woodhouse, 1969). Past research has shown that S fertilization of forage crops will not only increase forage yields, but it will also increase livestock performance (Rendig and Weir, 1959; Jones et al., 1982; Murphy et al., 1983). In Alabama the current recommendation is that all crops should receive 11 kg S per ha per year (Cope et al., 1983).

Phosphogypsum is a by-product of the phosphate fertilizer industry and substantial amounts are produced in Florida each year. It contains approximately 92% calcium sulfate (FIPR, 1983) and should be an excellent, relatively local source of S and Ca for forage production in the southeast. A series of field studies were conducted in south Alabama with the following objectives: 1) determine the influence of phosphogypsum on wheat forage yield and quality, 2) determine effects of tillage on yield and S fertilizer requirements and 4) determine if split S applications (fall vs. spring) will improve forage yield and quality.

EXPERIMENTAL METHODS

Field studies were initiated in southern Alabama during the fall of 1986 on a Benndale (coarse-loamy, siliceous, thermic, Typic Paleudults) and a Dothan (fine-loamy, siliceous, thermic, Plinthic Paleudults) soil (Table 1). Annual treatments applied to each site included two tillage methods, two N rates, five rates of S and two times of S application. Tillage methods were 1) turn-disk prior to planting (conventional) and 2) disk only prior to planting (reduced). For the conventional tillage treatment the soil was turned with a moldboard plow at a depth of 20 to 25 cm. Nitrogen was applied at rates of 134 and 202 kg ha^{-1} as ammonium nitrate. Sulfur was applied at rates of 0, 11, 22, 45 and 90 kg ha^{-1} as phosphogypsum (Table 2). An additional treatment received 45 kg S ha^{-1} as agricultural gypsum (Table 2). Sulfur was applied prior to planting (fall) or as a top dressing in early February (spring). Fall applications of S and half of the N was applied prior to the final disking operation. The remaining N was applied when the spring applications of S were made. The experiment was a split-plot design with 4 replications. Tillage methods were the whole plots. Nitrogen rates, S rates and time of S application were the split-plots. Split-plots were arranged as a randomized complete block within a tillage system.

TABLE 1

Initial chemical properties of the Dothan fine sandy loam and Benndale fine sandy loam soils receiving annual rates of phosphogypsum.

Location	Soil Series	Soil Depth	SO_4-S[#]	pH	Extractable Elements[&] Ca	K	Mg	P
		-- cm --	-mg/kg-		------ kg/ha			-------
Brewton	Benndale	0 to 25	6.1	6.2	713	65	81	67
Brewton	Benndale	25 to 51	16.3	5.2	280	52	63	5
Headland	Dothan	0 to 25	9.6	6.5	773	97	152	66
Headland	Dothan	25 to 51	14.5	5.8	325	45	64	3

[#] Extracted with a calcium phosphate solution.
[&] Extracted with Mehlich I (dilute, double acid) extractant.

TABLE 2

Composition of the phosphogypsum and agricultural gypsum applied as a source of S for wheat. Concentrations are given on an oven dry weight basis.

Source	S	Al	Ca	F	Fe	K	Mg	Na	P	Si
	-------					%				-------
Phosphogypsum[#]	15.3	0.12	20.8	0.98	0.14	1.61	0.01	0.12	0.65	3.58
Agric-gypsum[@]	15.7	1.03	20.6	0.03	0.37	0.26	0.63	0.24	0.01	0.71

[#] The phosphogypsum contained 21 pCi Ra-226 per gram.
[@] The agricultural gypsum contained 0.18 pCi Ra-226 per gram.

Wheat was planted in October or November of each year. 'Compton' wheat was planted at both locations in 1986-1987 and 'McNair 1003' wheat was planted in 1987-1988 and 1988-1989. Forage yields were determined as needed by mechanically harvesting a strip from each plot. Subsamples of forage were saved by plot from each harvest for chemical analysis. At the end of the study in 1989 soil samples were collected at depths of 0 to 25, 25 to 51, 51 to 76 and 76 to 102 cm. The samples were analyzed for extractable sulfate.

RESULTS AND DISCUSSION

As expected, wheat forage yields increased with the rate of N. On the Benndale soil, average forage yields were increased by an average of 13.3% by increasing the N rate from 134 to 202 kg ha^{-1} (Table 3). Averaged over three years, the 202 kg N ha^{-1} rate increased forage yields 18.6% as compared to the 134 kg N ha^{-1} rate on the Dothan soil (Table 3). The effect of tillage on forage yields was site dependent. On the Dothan soil, yields were affected by tillage during all three years of the study (Table 4). The conventional tillage system on the Dothan soil produced an average of 33.6% more wheat forage as compared to the reduced tillage system. On the Benndale soil wheat forage yields were affected by tillage during the third year of the study; During the third year of the study, average forage yields were 38% higher under conventional tillage (4631 kg ha^{-1}) as compared to the reduced tillage system (3352 kg ha^{-1}).

A response to added S (phosphogypsum) was observed during all three years of the study on the Dothan soil (Table 4) and during

TABLE 3

Wheat forage yields as affected by the rate of N applied to a Benndale and a Dothan soil during 1986-1989.

N Rate	1986-87	1987-88	1988-89
	kg/ha		
Benndale soil			
134	2645	4677	3668
202	2907	5226	4314
LSD(0.05)	156	189	181
Dothan soil			
134	2790	2558	3797
202	3600	3052	4189
LSD(0.05)	179	136	180

the first two years of the study on the Benndale soil (Table 5). In general, maximum forage yields occurred when 22 to 45 kg ha^{-1} S was applied, however, statistically no improvements were obtained beyond the 11 kg S ha^{-1} rate (Table 4 and Table 5).

The effect of time of S application (fall vs spring) was inconsistent and varied among sites. On the Dothan soil forage yields were affected by the interaction between tillage and time of S application ($P \leq 0.05$; data not shown). Analysis of these data showed that for the reduced tillage system higher yields were obtained by applying the S in the fall. On the Benndale soil, an average of 6% higher yields were obtained during the first two years of the study by applying S in the spring (Table 5).

TABLE 4

Effect of S rate (phosphogypsum) and tillage on wheat forage yields for the Dothan soil during 1986-1989.

Tillage	S rate, kg/ha					$\bar{X}$
	0	11	22	45	90	
	kg/ha					
Total Yields - 1986-1987						
Conventional	3409	3566	3174	3714	3698	$3512^{\$}$
Reduced	2606	2813	2837	3083	3051	2878
$\bar{X}^{\#}$	3007	3189	3006	3398	3374	
Total Yields - 1987-1988						
Conventional	2904	3217	3229	3308	3347	$3261^{\&}$
Reduced	2135	2520	2483	2531	2375	2409
$\bar{X}^{@}$	2520	2868	2856	2920	2861	
Total Yields - 1988-1989						
$\bar{X}^{*}$	3736	3975	4088	4191	3973	

\# S rate - LSD(0.05) = 283 kg/ha.
$ Tillage - LSD(0.05) = 194 kg/ha.
@ S rate - LSD(0.05) = 215 kg/ha.
& Tillage - LSD(0.10) = 632 kg/ha.
* S rate - LSD(0.05) = 285 kg/ha.

TABLE 5

Effect of S rate (phosphogypsum) and time of sulfur application on wheat forage yields for the Benndale soil during 1986-1988.

Time of S Application	S rate, kg/ha					$\bar{X}$
	0	11	22	45	90	
	kg/ha					
Total Yields - 1986-1987						
Fall	2487	2640	2678	2842	2683	2666[$]
Spring	2450	3018	2791	3093	3079	2886
$\bar{X}$[#]	2468	2829	2734	2968	2881	
Total Yields - 1987-1988						
Fall	4569	4844	4881	4979	5006	4856[&]
Spring	4693	5022	5185	5285	5069	5043
$\bar{X}$[@]	4631	4930	5033	5114	5037	

[#] S rate - LSD(0.05) = 246 kg/ha.
[$] Time - LSD(0.05) = 156 kg/ha.
[@] S rate - LSD(0.05) = 298 kg/ha.
[&] Time - LSD(0.10) = 158 kg/ha.

An additional set of treatments were included to compare agricultural grade gypsum with phosphogypsum. Statistical analysis of these data (Table 6) showed that wheat forage yields were not affected by the type of gypsum when S was applied to both soils at a rate of 45 kg ha^{-1}.

TABLE 6

Effect of phosphogypsum and Agricultural grade gypsum on total wheat forage yields when applied at a rate of 45 kg S ha^{-1}.

Soil	Year	Type of Gypsum	
		Phosphogypsum	Agricultural
		kg/ha	
Benndale	1986 - 1987	2827	2968
	1987 - 1988	5134	5036
	1988 - 1989	4008	3933
Dothan	1986 - 1987	3398	3233
	1987 - 1988	2920	2929
	1988 - 1989	4191	4025
	$\overline{X}$	3746	3687

LSD(0.05) = Nonsignificant

Wheat forage from each harvest was analyzed for N and S. The data presented in Table 7 are representative of the test. In general, the concentration of S increased and the N:S ratio decreased with increasing rates of added S. Maximum crop yields have been associated with a N:S ratio in plant tissue ranging from 14:1 to 19:1 (Bull, 1971; Metson, 1973; Reneau and Hawkins, 1980; Stewart and Porter, 1969; Tisdale, 1977). However, ruminants require a N:S ratio of 10:1 to 12:1 for optimum performance (Allaway and Thompson, 1966; Moir et al., 1967-1968; Murphy et al., 1983; Rendig and Weir, 1957; Tisdale, 1977). The data in Table 7 and Table 5 indicate that a higher quality forage was being produced when S was applied at rates that were higher than that needed for optimum yields.

TABLE 7

Effect of S rate (phosphogypsum) on the concentration of S and N/S ratios in wheat forage for the Benndale soil in 1986-1987.

S rate	Forage S Concentration	N/S ratio
kg/ha	----- % -----	
0	0.11	19.2[#]
11	0.14	15.1
22	0.14	14.7
45	0.16	12.4
95	0.18	10.8
LSD(0.05)	0.01	1.7

[#] The concentration of N was not affected by the rate of N ($P \leq 0.05$) during 1986-1987.

During the final year of the study, selected soil and plant samples were analyzed for Ra-226 (Table 8). The phosphogypsum contained low levels of this isotope (Table 2). Results of these analyses demonstrate that fertilizer rates of phosphogypsum have little if any effect on the level of Ra-226 in the soil or harvested forage. Intensive soil sampling of the conventional tillage system showed that a majority of the applied S may have leached out of the rooting zone in both soils (Table 9).

TABLE 8

Radiological analysis of selected soil and wheat forage samples as affected by the rate of sulfur added as phosphogypsum. Forage samples are for the first harvest during the 1988-1989 season and soil samples were collected at the end of the field studies in 1989.

Sulfur	Soil Depth, cm				Forage
Rate	0 to 25	25 to 51	51 to 73	76 to 102	Ra-226
kg/ha	pCi Ra-226/g				pCi/g
			Brewton		
0	0.15	0.10	0.10	0.23	0.13
22	0.15	0.18	0.18	0.10	0.10
45	0.10	0.15	0.10	0.08	0.10
LSD(0.05)	NS	NS	NS	NS	NS
			Headland		
0	0.25	0.25	0.23	0.35	0.10
22	0.30	0.23	0.23	0.33	0.15
45	0.25	0.18	0.20	0.28	0.18
LSD(0.05)	NS	NS	NS	NS	NS

TABLE 9

Effect of phosphogypsum (S rate) on extractable sulfate in the conventional tillage system on the Benndale and Dothan soil. Samples were collected at the termination of the field studies in 1989.

	S rate, kg/ha					
Soil Depth	0	11	22	45	90	LSD(0.05)
--- cm ---	mg/kg					
Benndale soil						
0 to 25	8	8	7	9	9	NS
25 to 51	16	18	17	19	26	4
51 to 76	22	24	29	32	34	3
76 to 102	25	23	23	26	31	3
Dothan soil						
0 to 25	14	11	9	11	14	NS
25 to 51	13	15	15	18	25	4
51 to 76	30	36	34	43	51	9
76 to 102	79	92	94	100	108	15

CONCLUSIONS

The results from this three year field study on two sandy soils in the Coastal Plain of Alabama demonstrate that phosphogypsum is an acceptable source of S for annuals grown for forage. Sulfur applied as phosphogypsum increased the yield and quality of wheat harvested for forage. The results demonstrate that phosphogypsum and agricultural grade gypsum produced the same forage yields. The effect of applying S as phosphogypsum in the fall or the spring was site dependent. There was no interaction between the rate of S and the rate of N or tillage system. The application of S did not overcome the detrimental effects of the reduced tillage system. Analysis of selected soil and wheat forage samples suggest that phosphogypsum (when applied at fertilizer rates) has little effect on the concentration of Ra-226 in the soil or harvested forage.

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BENEFICIAL EFFECTS OF GYPSUM FOR PEANUT

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ABSTRACT

Adequate availability of calcium (Ca) in the upper 8 cm of soil is necessary for pod development and for production of high quality peanut (*Arachis hypogaea* L.). Calcium is absorbed directly by the pod and is not translocated to the pod via the above-ground plant. Therefore, high soil solution Ca must be maintained in the upper 8 cm of soil for a period that may extend for 65 days following the entrance of pegs into the soil and the initiation of pod development. Field and laboratory experiments were conducted to determine the best Ca source(s), timing and rates of application, and the relation of Ca to other cations in the soil solution. Phosphogypsum amendment resulted in high peanut yield and quality in comparison with other Ca source amendments. Gross return response from the application of 224 kg Ca/ha as phosphogypsum was $986/ha in one experiment. Major benefits of gypsum amendment were attained on sandy soils that did not have adequate sorbed Ca to replenish the soil solution Ca following a rainfall or irrigation that leached Ca from the upper 8 cm. In such soils, bloom time applications were more effective than planting time applications. Some of the observed benefit appeared to be due to a gypsum-induced solubilization of K and Mg; thus making those elements more subject to leaching; and thereby attaining a higher and more desirable ratio of Ca/(K + Mg) which in turn lead to less pod rot and higher peanut production and quality.

INTRODUCTION

Peanuts (Arachis hypogaea L.) are very unique plants in their development. The seed pushes up from the soil during germination; following vegetative growth and flowering, pegs are sent back to the soil for underground seed development. An adequate concentration of calcium (Ca) in the upper 8 cm of soil is extremely important for pod development and subsequently for high yields and grades of the crop, Cox et al. (1982). Under low Ca concentrations nuts will not develop and/or they will have high incidences of dark plumules and pod rot which result in low yield and grade. When soil Ca concentrations are below threshold levels amendments are needed in order to replenish the Ca in the soil solution. Substantial evidence exists to show that the Ca must be in solution in the pod development area of the soil, since the plant does not translocate adequate quantities through the peg. Therefore, root uptake is not effective in supplying the needed calcium. Studies indicate that Ca is accumulated in the pod via diffusion through the hull containing the developing nuts (Sumner et al., 1988).

Gypsum is an effective calcium source for application to peanuts when Mehlich 1 extractable soil Ca is less than 560 kg/ha (Mehlich, 1953). It is commonly broadcast at rates of 500 to 1000 kg/ha at first flowering of the crop. Its popularity is due to its greater solubility than limes and its neutral reaction with the soil solution (normally having little effect on soil pH). The literature concentrates on the supply of Ca from gypsum. However, some studies have also indicated that the ratios of Ca with potassium (K) and magnesium (Mg) are also of importance, Comber (1959), Wolt and Adams (1979). Therefore, the leaching of K and Mg from the upper 8 cm by exchange for Ca in $Ca\ SO_4$ could also affect peanut production. Recent studies reviewed here have involved:

1. The comparison of gypsum sources,
2. Effects of timing and rate of gypsum,
3. Effects of soil Ca concentrations and ratios with soil K and Mg on peanut yield grade and value, and
4. Effects of gypsum on relative concentrations of Ca, K and Mg in the soil.

MAIN TEXT

COMPARISONS OF GYPSUMS FOR SUPPLYING POD ZONE CALCIUM.

Laboratory and field experiments were conducted to compare the solubility of phosphogypsum with other sources of gypsum commonly applied to peanuts and to compare the effectiveness of the sources for peanuts (Alva et al. 1989).

Laboratory study

The forms and total Ca contents of the seven commercially-available gypsum materials evaluated in this study are shown in Table I. Total Ca of each gypsum material was determined by dissolving duplicate samples of one gram each of gypsum material in 100 ml of 3 M HCl. The concentration of Ca in the extract was measured by atomic absorption spectroscopy.

TABLE I. Forms and total contents of gypsum materials.

Gypsum materials	Ca content -----%----
Fine powder (dry)	20.5
Phosphogypsum	19.7
Coarse powder	20.2
Granular	17.8
Granular	17.0
Pelleted	20.8
Crystalline	20.6

Recovery of Ca from the seven gypsum materials in either Mehlich 1, a weak salt solution (0.01 M $NaNO_3$) or deionized water was studied. Triplicate 0.4 g samples of each gypsum material were transferred to a 0.5 L polystyrene bottle and 0.5 L of the extractant was added. The bottles were shaken for 4 h on a vibrating shaker. The suspension was allowed to settle for 4 h and the supernatant was filtered through Whatman 42 filter paper. Concentration of Ca in the filtrate was determined by atomic absorption spectroscopy. Calcium recovered in each extractant was calculated as a percentage of total Ca in the gypsum materials.

A wide extractant to gypsum ratio (1250:1 v/wt) was employed in order to assure that gypsum solubility was not limiting the recovery of Ca. Recovery of Ca in the Mehlich 1 extractant was >96% except for the two granular sources (Fig. 1). Recovery of Ca with the Mehlich 1 extractant was significantly greater than that with either 0.01 M $NaNO_3$ or deionized water for all the gypsum materials except dry fine powder. For the phosphogypsum, one granular and the pelleted gypsum, there were no significant differences between the recoveries with 0.01 M $NaNO_3$ or deionized water. Recovery of Ca in deionized water was >96% of total Ca for phosphogypsum and the two powdered sources. For all other gypsum sources, the recovery of Ca was 5-13% higher with the Mehlich 1 extractant than with 0.01 M $NaNO_3$ solution.

Field study

Effects of the seven gypsum materials on soil test Ca levels and on peanut yield were investigated in Lakeland sand (thermic, coated typic Quartzipsamments) with a pH of 6.0 and Mehlich 1 extractable K, Mg and Ca of 39, 40 and 127 kg/ha, respectively. The site of the experiments was previously fallow for 1 year preceded by peanut.

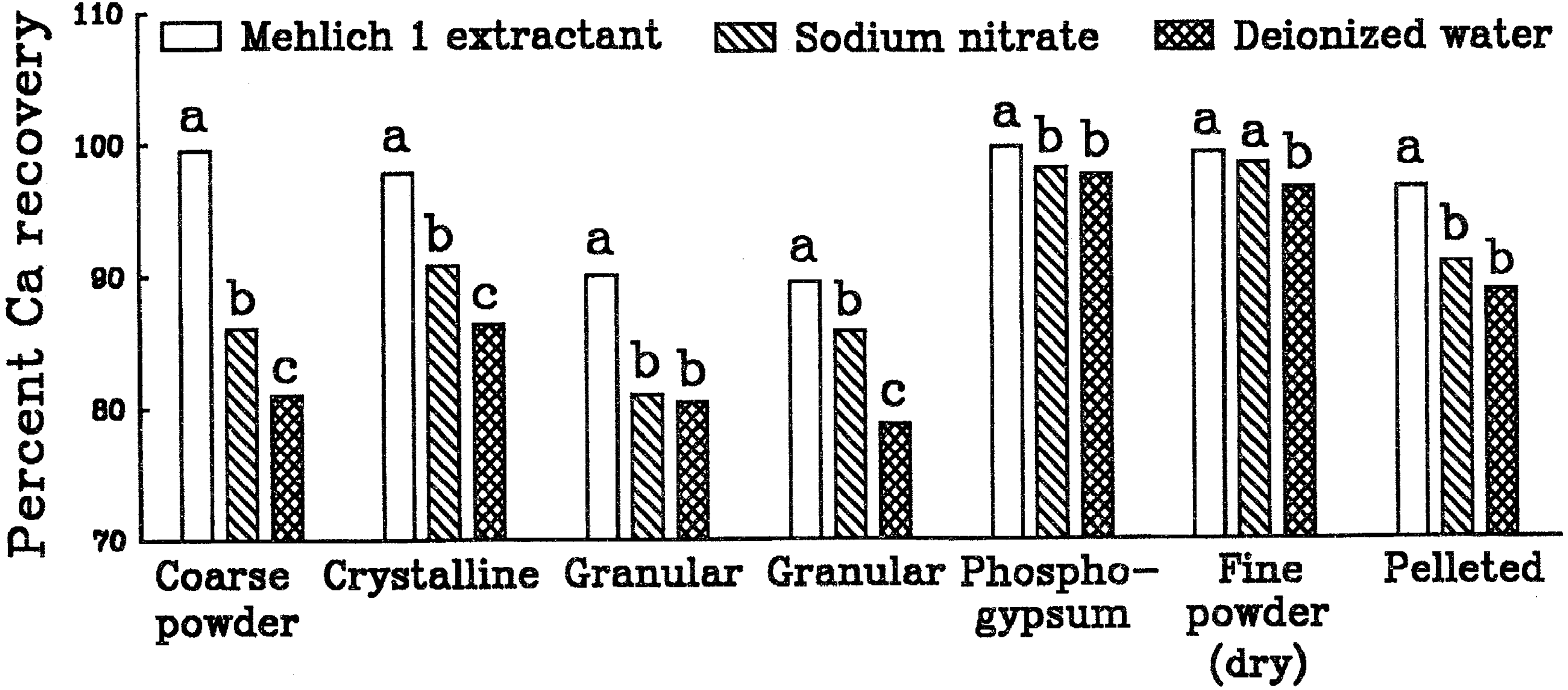

Fig 1. Calcium in gypsum solubilized by three extractants.

No fertilizer other than Ca treatments was applied. Recommended practices of land preparation and incorporation of herbicide and nematicide were followed. Florunner peanut was planted in 91 cm rows (112 kg seed/ha). The experiment was conducted with 3 replications.

Gypsum materials were broadcast at first bloom, 50 d after planting, to supply 224 kg Ca/ha. The quantity of gypsum required was calculated on the basis of percent total Ca (Table I) in each of the seven materials. Soil samples were taken, O-8 cm deep,from both gypsum and control plots prior to application of gypsum and at 12 weekly intervals following application of treatments.

Peanuts were dug (1.82 x 8.21 m plots) with a mechanical digger-shaker-inverter, and combined 6 d later. Pod yield was calculated at 7% moisture. A 500 g pod sample was used to determine quality parameters which included sound mature kernels (SMK) according to Federal-State Inspection Service guidelines. Gross return/ha was calculated by multiplying pod yield/ha and price per ton based on the grade data.

Soil samples were air dried, and screened to pass a 2-mm sieve in preparation of Ca determination. Twenty ml each of Mehlich 1 extractant or 0.01 M $NaNO_3$ solution was added to 5 g of each soil and shaken for 10 min. The supernatant was filtered through Whatman 42 filter paper and concentration of Ca in the filtrate was measured by atomic absorption spectroscopy.

Application of crystalline, phosphogypsum, coarse powder, or fine dry powder gypsums to the soil all resulted in the highest pod yield and gross return (Table II). Gross return for the application of phosphogypsum was $986/ha greater than for the control. However, there were no, significant differences in the above parameters among several sources. Compared to control, gross return for peanuts sold within the quota program increased by

1101 $/ha or $986 where crystalline or phosphogypsum gypsum were applied, respectively, however the increase was only 68-83 $/ha for one granular and the pelleted gypsum treatments. Gross return was greater by 903-918 $/ha for phosphogypsum gypsum treatment than for one granular or the pelleted gypsum treatments. Percent SMK in gypsum treatments was greater than in the control treatment by 6 to 9%, regardless of the type of material applied.

TABLE II. Effects of various gypsum materials on pod yield, grade and gross return.

Gypsum materials	Pod yield[1]	SMK[2]	Gross return[3]
	kg/ha	%	$/ha
Crystalline	4480a[4]	70a	3134a
Phosphogypsum	4387ab	69a	3019ab
Coarse powder	4107abc	68a	2812abc
Fine powder (dry)	3862abc	68a	2624abcd
Granular 1	3462abc	70a	2400bcd
Granular 2	3302bc	68a	2116cd
Pelleted	3100c	67a	2101d
Control	3033c	61b	2033d

[1] Pod yield adjusted to 7% moisture.

[2] Percent sound mature kernels.

[3] For quota peanuts according to the USDA Peanut Loan Schedule, 1988.

[4] The means followed by similar letters for each soil are not significantly different at $P = 0.10$.

Since the cost of phosphogypsum applied at Tifton, Georgia averages only one-third of the cost of the other materials, it is fairly evident why it is a preferred source where it is available.

Prior to application of gypsum to the Lakeland soil Mehlich-1 and 0.01 M $NaNO_3$-extractable Ca ranged from 94 to 170 and 24 to 45 kg/ha, respectively (Fig. 2). Application of the wet fine powder form resulted in the greatest increase in Mehlich 1- and 0.01 M $NaNO_3$-extractable Ca within 6 and 14 d

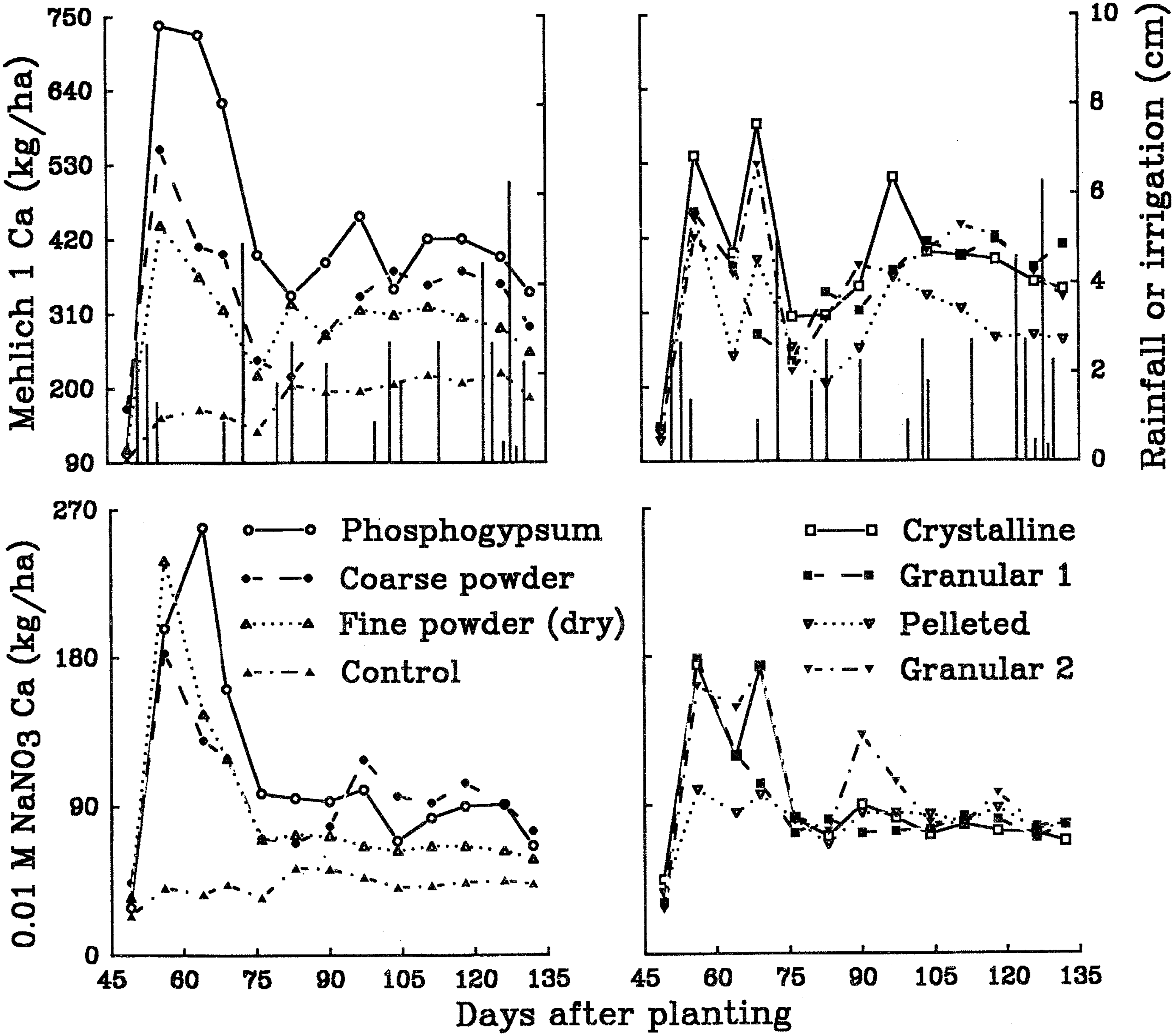

Fig. 2. Soil calcium determined by two extractants as affected by time following gypsum application.

after application, respectively. Soil test Ca levels were high until 69 d after planting thereafter the levels decreased following excessive rainfall at 72 d. The decrease was particularly dramatic where powdered sources of gypsum were applied. Six days after application of gypsum, Mehlich 1 Ca was significantly greater in soil treated with phosphogypsum as compared to all the other gypsum materials. However, 0.01 M $NaNO_3$ extractable Ca was much higher in the treatments receiving fine powder forms of gypsum than in those receiving pellets or granular forms. This difference decreased considerably for the later samples. One hundred and thirty-two days after planting, Mehlich 1 Ca ranged from 254-410 kg/ha in gypsum amended treatments, regardless of source of gypsum, as compared to 187 kg/ha in control treatment.

Experiments comparing solubility, calcium supplying power, and effectiveness of gypsums for peanut clearly indicate that phosphogypsum is a preferred source, especially when costs to the farmer are a consideration.

EFFECTS OF TIMING OF GYPSUM AND POTASSIUM AND MAGNESIUM APPLIED

Sandy soils with low cation exchange capacities often have low Ca concentrations in the upper 8 cm due to losses by leaching. Questions have always arisen concerning the possible need for repeat gypsum applications when rainfall is heavy following the bloom application. The current recommendations in Georgia are to broadcast 160-200 lb Ca as gypsum to runner peanuts when Mehlich 1 extractable Ca is <560 kg/ha in the top 8 cm 10-14 days after planting. For Virginia peanuts the rate should be double regardless of soil test (Plank, 1989). In order to determine the need for split applications three experiments were conducted in 1988 and 1989. In 1988 we experienced 3 cm of rainfall during the 3 weeks following a bloom application and in 1989 we had 14 cm. Therefore, the 1989 experiment presented the best opportunity for testing the need for reapplication. The combination of the very sandy soil (Lakeland s with 0.6% o.m., pH = 6.9 and 21, 325 and 66 kg/ha Mehlich 1 extractable K, Ca and Mg, respectively, and 0.50 $\mathrm{cmol_c/kg}$ CEC) with the excessive rainfall provided as severe of conditions as have occurred in the Coastal Plain peanut belt during the past 10 years. Therefore the 1989 data are presented here.

The experiment was a split-split arrangement of randomized complete block design with five replications. Main plots were type of peanut (runner or Virginia).The runners were Florunner and the Virginias were GK3. Subplots were fertility level, either "high" or "low" for K and Mg. Low refers to recommended fertilization according to the Georgia Extension Service (Plank, 1989). High was low plus 1120 kg/ha of sulphate of potash magnesia, supplying an extra 246, 246, and 112 kg/ha of K_2O, S and Mg, respectively. Sub-sub plots were the gypsum treatments shown in Table III and consisted of 1. control, 2. 1120 kg incorporated to 8 cm prior to planting, 3. applied at first bloom (recommended), 4. applied in 2 applications at bloom and bloom plus 3 weeks,5. 2240 kg/ha applied at first bloom and 6. applied split as in treat. 4. All cultural practices were standard for Georgia except for the Ca treatments.Measurements were made for yield, grade and pod rot. Value of the crop was calculated from the 1989 USDA formulae.

Analysis of variance indicated significant differences between peanut types. Also for some variables the interaction of fertility level with Ca treatments is significant. Therefore, the interaction data are shown in Table III. The general trends in the data are that Virginia peanuts responded more to Ca treatments than runners, that high K and Mg additions were detrimental to peanut yield, grade, value and increased pod rot; and that the best improvements were made for split applications > single bloom applications >

Table III. Effect of Peanut type, fertility level and rate and timing of gypsum application on grade, yield, value and pod rot, Lakeland s., 1989.

A. Runner

Fertility	Treatment	Pod Yield	SMK	Value	Pod rot
		kg/ha	%	$/ha	%
High	1. No Gypsum	4658b	66c	3112c	3.5a
	2. Spring Gyp	5375ab	72b	3796bc	0.8b
	3. Gypsum	5723a	74ab	4150ab	1.0b
	4. Gyp 2X	5471ab	74ab	4004ab	1.0b
	5. Gyp Split	6150a	75a	4510a	0.5b
	6. Gyp 2X Split	5501ab	75a	4048ab	0.8b
Fertility mean		5516B	72A	3972B	1.2A
Low	1. No Gypsum	5635ab	72c	3992b	1.8a
	2. Spring Gyp	5628ab	73b	4083b	1.8a
	3. Gypsum	5609b	76a	4159b	1.2a
	4. Gypsum 2X	5783ab	75a	4283ab	1.0a
	5. Gyp Split	5900ab	74b	4263ab	0.0a
	6. Gyp 2X Split	6332a	76a	4733a	0.8a
Fertility mean		5815A	74A	4253A	1.1A

B. Virginia

Fertility		Pod Yield	SMK	Value	Pod rot
		kg/ha	%	$/ha	%
High	1. No Gypsum	2131b	45c	1032b	11.5a
	2. Spring Gypsum	5195a	60b	3532a	2.5b
	3. Gypsum	5687a	65a	3950a	1.8b
	4. Gyp 2X	5692a	66a	3952a	0.2b
	5. Gyp Split	5226a	65ab	3577a	2.2b
	6. Gyp 2X Split	5484a	66a	3866a	0.5b
Fertility mean		5023B	61B	3379B	3.1A
Low	1. No Gypsum	4630b	59b	2924c	4.8a
	2. Spring Gypsum	5378a	64a	3621b	1.3b
	3. Gypsum	5907a	66a	4179a	1.0c
	4. Gypsum 2X	5671a	66a	3903ab	3.8ab
	5. Gypsum Split	5274ab	67a	3735ab	2.5abc
	6. Gyp 2X Split	5462a	66a	3853ab	0.0c
Fertility mean		5387A	64A	3703A	2.3B

spring applications > no gypsum. However, not all of these trends are statistically significant. Since value/ha is the most important variable and is dependent on pod yield and % SMK which in turn are partially dependent on pod rot, it deserves further analysis. Value/ha for the runner peanut was decreased significantly by high K and Mg fertility. At the high fertility level all Ca treatments except spring incorporated gypsum significantly increased value/ha. Splitting and doubling the application didn't increase value above a single bloom application of 1120 kg/ha. At the low fertility level response to gypsum was much less, only the 2240 kg/ha gypsum rate split to two applications increased yield significantly above no gypsum, spring gypsum and application of 1120 kg/ha at bloom. The value/ha of Virginia peanuts was also reduced significantly by high K and Mg additions. Responses to gypsum were great and statistically equal regardless of the timing or rate. Response was due in some large part to a reduction in pod rot by any gypsum application. At the low fertility level, Virginia peanut value was also increased above no gypsum for all gypsum timings and rates. Application of 1120 kg/ha of gypsum at bloom resulted in more value than that rate incorporated in the spring. Doubling the rate and splitting the application rate had no significant effect on value/ha.

Since our experiments were conducted under extreme leaching conditions, as well as with normal and excessive K and Mg levels, we believe that responses to high rates and splitting of gypsum applications were more likely in this test than in commercial culture. Therefore, we concluded that rates higher than recommended (1120 kg/ha broadcast at first bloom) and splitting of gypsum applications are not likely to be economically sound practices in commercial peanut production fields. Presently the double rate applied at bloom is recommended for Virginia peanuts in Georgia, these data do not support the need for the double rate (2240 kg/ha broadcast) even for the Virginia peanut. The results also clearly show the detrimental effects of high Ca and Mg for both types of peanuts.

EFFECTS OF GYPSUM ON POTASSIUM AND MAGNESIUM IN THE PEANUT PEGGING ZONE.

A considerable body of evidence shows that high K and/or Mg increases pod rot and decreases peanut yield and grade. The objective of this experiment was to determine the differential leaching of K and Mg by a gypsum responsive soil of the lower Coastal Plain and a nonresponsive soil of the upper Coastal Plain.

Two soils representing upper (Greenville s.c.l.) and lower (Tifton l.s.) Coastal Plain soils of the peanut belt of Georgia were selected to study the effects of gypsum amendment on leaching of K and Mg from the top 8 cm of soil. Soil samples were collected at a depth of 0-15 cm, air-dried, ground and sieved through a 2 mm sieve. Important physico-chemical properties of the two soils are given in Table IV.

Table IV. Physico-chemical characteristics of soils evaluated for leaching of potassium and magnesium.

			Particle size analysis			Exchangeable[2] cations				Σ
Soil	pH[1]	Organic matter	sand	silt	clay	Ca	Mg	K	Na	Cations
		-----------g/kg----------				-----------cmol$_c$/kg-----------				
Tifton sand	5.7	6.2	890	70	40	0.36	0.10	0.09	0.01	0.56
Greenville sandy clay loam	6.9	14.7	680	80	240	2.50	1.12	0.06	0.02	3.70

[1] Measured by glass electrode in 1:1 soil:water ratio

[2] Measured in 0.2 M NH_4Cl

Twenty mL of 0.2 M NH_4Cl was added to 5 g soil and shook for 30 min followed by centrifugation for 10 min and filtration through Whatman No. 42 filter. Concentrations of Mg, and K were determined by atomic absorption spectroscopy. Concentrations of extractable cations were also determined in Mehlich 1 extractant (Mehlich 1953).

The soil was packed to a height of 8 cm height in PVC columns (7 cm inner diameter and 9 cm height) to attain a bulk density of 1.37 for the Greenville soil (pore volume = 142 mL) and 1.60 for the Tifton soil (pore volume = 116 mL). Finely divided dry gypsum (0.43 g) 1120 kg ha^{-1}) was uniformly spread on the surface of the soil and a filter paper was placed to facilitate uniform distribution of water on the soil surface column during leaching. Two columns with no gypsum were leached as controls. Application of water on the top of the filter paper was by using a peristaltic pump at the rate of 1.5 mL min^{-1}. Leachate was collected using a separate measuring cylinder for each pore volume. Leachate pH and electrical conductivity (EC) were measured. A subsample of each leachate was filtered through 0.45 µm membrane filter and concentrations of Mg and K were determined by atomic absorption spectroscopy.

Application of gypsum on the surface of soil columns resulted in greater leaching of K and Mg than in unamended soils (Fig. 3). This difference was very marked in the Tifton soil as compared to the Greenville soil. In the former soil, the percentages of Mehlich 1-K and -Mg leached in the first pore volume of leachate were 2 to 4 and 4 to 15 fold greater, respectively, in gypsum amended soil than that in unamended soil. Following the leaching of 580 mL of water through gypsum amended soil columns, 88 and 78% of the Mehlich 1 extractable K and Mg, respectively, were leached in the Tifton soil as compared to 34 to 44% of K and 26% of Mg leached in the Greenville.

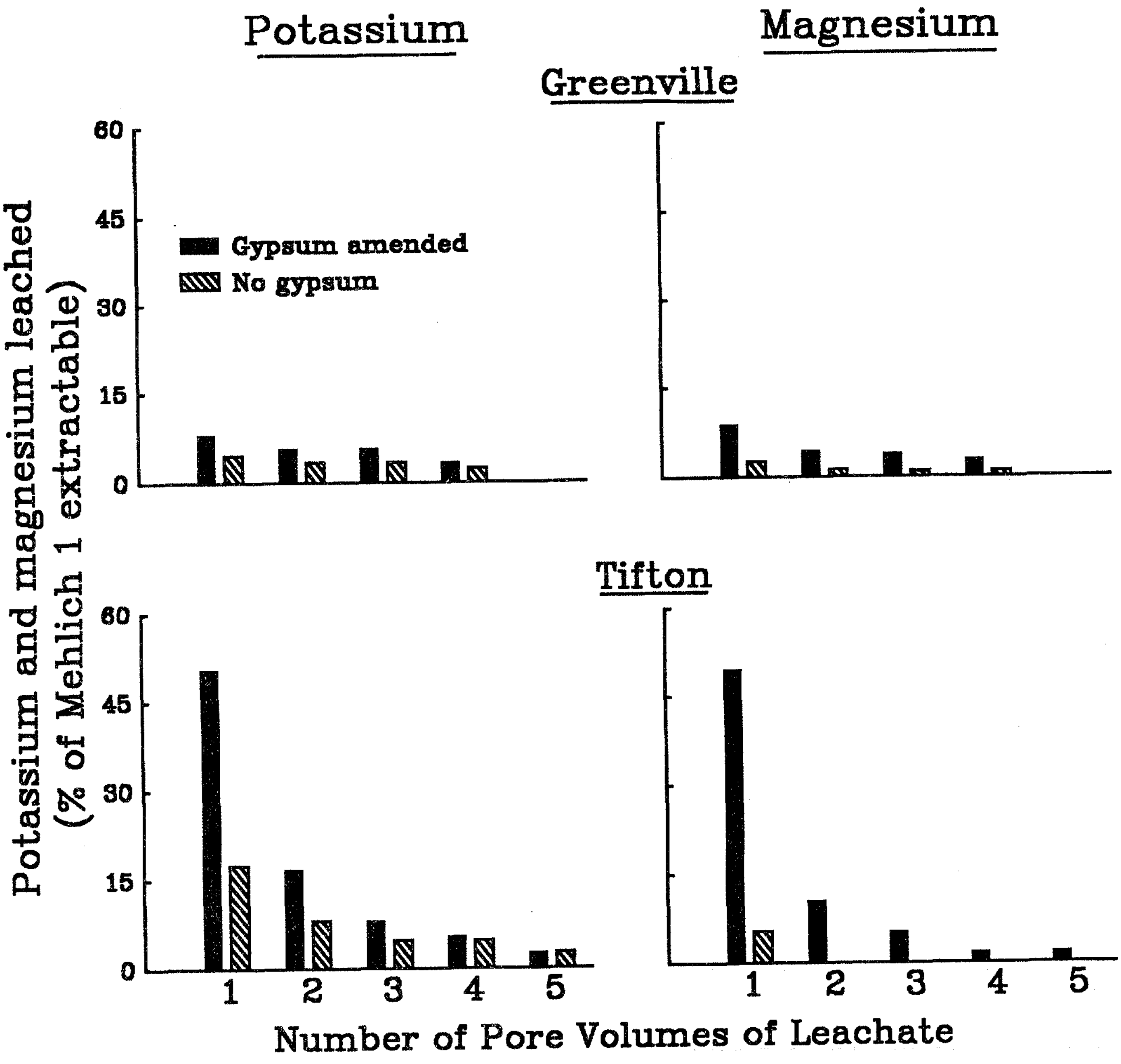

Fig. 3. Potassium and magnesium leached as affected by soil and gypsum amendment.

Influence of gypsum in depletion of K and Mg in topsoil has been demonstrated by O'Brien and Sumner (1988), and Syed (1987). Such an effect was presumably due to competitive exchange of K and Mg by Ca and subsequent leaching of the former cations from the topsoil.

Greater depletion of K and Mg in the top 8 cm soil, which represents the fruiting zone of peanut, in gypsum amended as compared to unamended soil may be beneficial for peanut pod development and ultimately the grade and yield of peanut. Brady et al. (1948) have shown a decrease in pod filling with an increase in concentration of K in the fruiting zone. Increased Ca status in the fruiting zone alleviated the adverse effects of high concentration of K. Although Brady et al. (1948) have not identified the role of increased Ca in overcoming the adverse effects of high concentration of K, it appears that depletion of K from the fruiting zone by increased Ca addition was partly responsible. Adverse effects of high K on peanut yield were also demonstrated in several field experiments (Anderson 1970; Chesney 1975; Hall 1975; Sullivan et al. 1974; Walker 1975). Recent studies of Csinos and Gaines (1986) and Csinos et al. (1984) have shown that high K and/or Mg in the fruiting zone increased percent pod and decreased percent sound mature kernels and yield.

In view of the above evidence of adverse effects of high K and/or Mg on peanut quality and yield, it appears that the beneficial role of gypsum on peanut pod development is partly due to removal of excess K and/or Mg from the fruiting zone, thus maintaining a more favorable cation balance required for adequate pod development. Indeed, gypsum-induced leaching of K and Mg was greater in sand than in the sandy clay loam. The response to gypsum application as a source of supplemental Ca is more pronounced in the former than in the latter soil. Low Ca status of the sandy soils obviously is the primary factor for response to gypsum application. However, a pronounced leaching of K and Mg from the fruiting zone as a result of gypsum application is also a contributing factor for decreased pod rot and improved grade and yield of peanut.

CONCLUSIONS

Phosphogypsum is a valuable source of Ca for peanuts when applied at bloom to peanut soils with less than 560 kg/ha of Mehlich 1 extractable Ca in the top 8 cm, 10 to 14 days after planting. No other source of gypsum exceeded phosphogypsum in solubility, or in its beneficial effects on peanut yield and grade. In much of the peanut belt of Georgia the cost of applied phosphogypsum is approximately one-third of the other gypsum sources commonly used. Thus its application can result in substantially less cost to the peanut farmer. Beneficial effects are due to increased Ca levels in the pod zone during pod development and also to increased movement of K and Mg from the pod zone thereby increasing the Ca/(K+Mg) ratio.

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