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**EVALUATION OF POTENTIAL COMMERCIAL
PROCESSES FOR THE PRODUCTION OF
SULFURIC ACID FROM PHOSPHOGYPSUM**

FINAL REPORT

**PREPARED BY ZELLARS-WILLIAMS, INC.
UNDER A GRANT SPONSORED BY THE
FLORIDA INSTITUTE OF PHOSPHATE RESEARCH
BARTOW, FLORIDA**

October, 1981

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FLORIDA INSTITUTE OF PHOSPHATE RESEARCH

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PRODUCTION OF SULFURIC ACID FROM PHOSPHOGYPSUM**

FINAL REPORT

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ABSTRACT

Phosphogypsum is a synthetic by-product created during the commercial manufacture of phosphoric acid by the wet process. The synthetic phosphogypsum retains the basic chemical and physical properties of natural gypsum and can be substituted for natural gypsum in the manufacture of a variety of commercial products. The commercial incentives which justify the exploitation of by-product phosphogypsum in nations which lack domestic gypsum sources and seek to avoid expensive imports are absent in Florida. As a result, phosphoric acid producers in Florida consider phosphogypsum a process waste requiring permanent disposal. Approximately 30 million tons are added each year to the more than 300 million tons of phosphogypsum currently stockpiled in Florida. At that rate, the volume of waste gypsum stored in Florida will triple by the year 2000. The reduction of gypsum disposal requirements through commercial exploitation of by-product phosphogypsum has been assigned a high priority by the Florida Institute of Phosphate Research (FIPR). This report documents the technical feasibility of substituting synthetic phosphogypsum for the natural gypsum used in an experimental process which recovers the commercial sulfur values liberated by, the thermal decomposition of natural gypsum.

INTRODUCTION

Phosphate rock is the primary commercial source of phosphorus, an essential and irreplaceable ingredient in high-yield agricultural fertilizers. Phosphate rock is insoluble in its natural state and the phosphorus values contained in the rock are unavailable as plant nutrients. The rock must be converted to a soluble form prior to the manufacture of finished fertilizers. Wet process phosphoric acid plants are the most common means of converting phosphate to a soluble form. The principal chemical reaction that occurs during the wet process is the digestion of tricalcium phosphate using concentrated sulfuric acid. The reaction yields a dilute phosphoric acid solution and synthetic gypsum crystals.

The reaction occurs when ground phosphate rock is continuously fed into an agitated reactor containing concentrated sulfuric acid, unattacked phosphate rock, recycled phosphoric acid, and gypsum crystals. Free sulfuric acid dissolves tricalcium phosphate to yield a dilute phosphoric acid solution and hydrated calcium sulfate. The acid solution is filtered to remove crystallized gypsum and then evaporated to increase concentration. Gypsum crystals trapped on the acid filter are collected and removed in a separate process stream, Figure 1 is a simplified block flow diagram illustrating the wet process.

Although phosphogypsum is a by-product, each ton of P_2O_5 produced by the wet process results in approximately 5 tons of waste gypsum. The impact of this curious production paradox is mitigated somewhat in nations which lack domestic gypsum sources and seek to avoid expensive imports. Phosphogypsum retains the basic chemical and physical properties of the natural gypsum used to manufacture commercial products for the agricultural, construction and chemical industries. The synthetic gypsum can frequently be substituted for natural gypsum in many of these manufacturing processes. As a result, the commercial exploitation of by-product gypsum is common among foreign acid producers such as Japan and South Africa who lack adequate domestic supplies of natural gypsum. Japanese companies routinely utilize phosphogypsum in the manufacture of building blocks and wallboard for the construction industry. Phosphogypsum is thermally decomposed in South Africa to produce sulfur dioxide and cement clinker.

The abundance of inexpensive natural gypsum in the United States has prevented the commercial exploitation of by-product phosphogypsum by the three industries which consume natural gypsum. The domestic agricultural markets which could conceivably consume some portion of the phosphogypsum produced in Florida are located far from the source and are not likely to absorb the expense of transporting phosphogypsum great distances. The widespread availability of natural gypsum restricts the use of phosphogypsum by the construction industry to very narrow local markets capable of consuming only a small portion of annual waste gypsum product ion. The chemical industry is capable of converting the sulfur dioxide gas generated by the thermal decomposition of gypsum to commercially acceptable sulfuric acid, the leaching agent wet process acid producers commonly rely on to convert phosphate rock to a soluble form. Sulfuric acid is also used in a variety of other industrial and manufacturing processes and is increasing in value as sulfur costs rise while supplies dwindle. Recovering sulfur dioxide gas from the thermal decomposition of gypsum is a

DAP - DIAMMONIUM PHOSPHATE
 GTSP - GRANNULAR TRIPLE SUPERPHOSPHATE

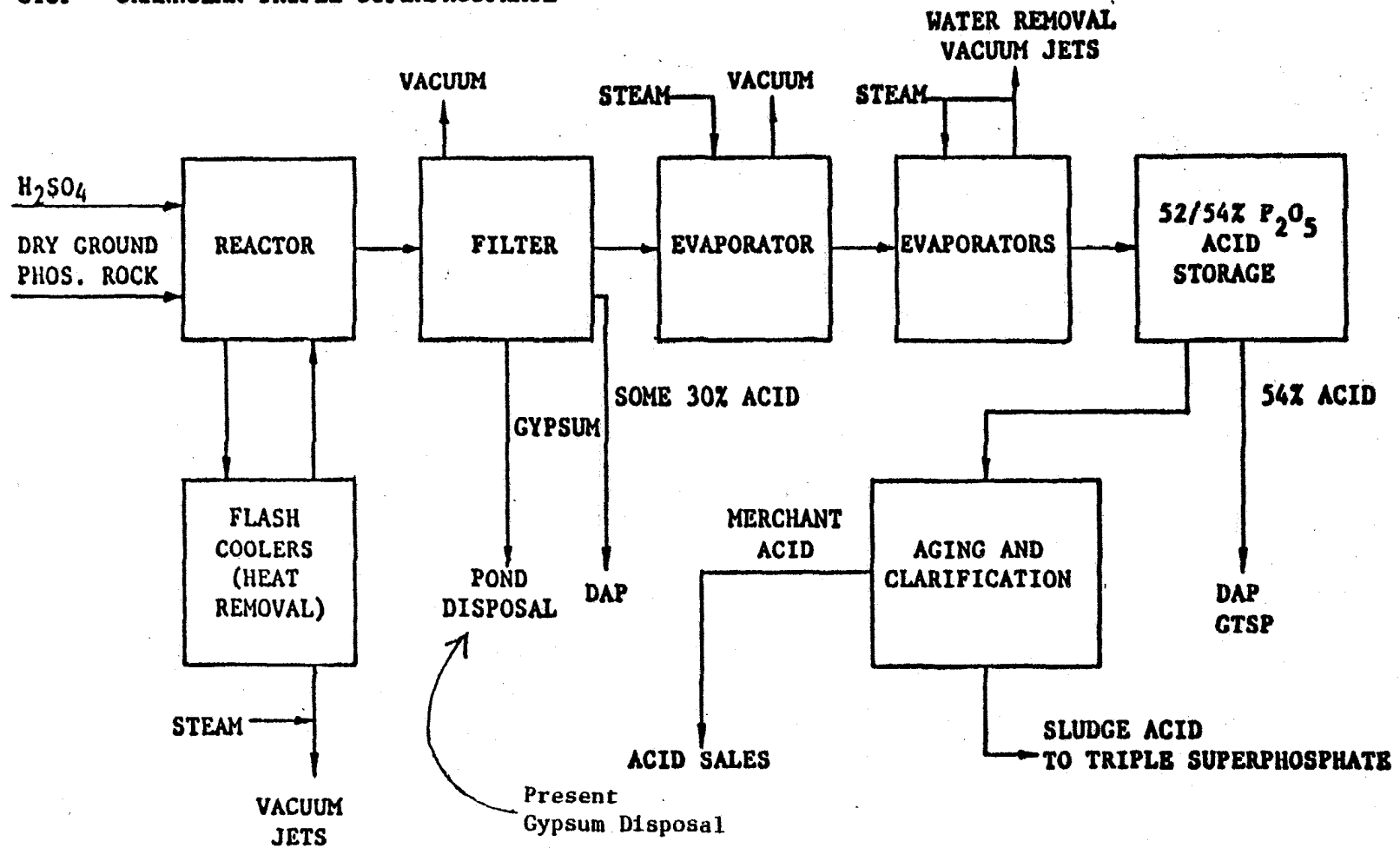


Figure 1 - Wet process phosphoric acid.

technically feasible alternate source of sulfur, but the prevailing economics of conventional processes are currently unfavorable. Thermal decomposition is an energy intensive process that commonly relies on the ignition of expensive, petroleum-based fuels to generate the temperatures necessary for decomposition. While such economics remain prohibitive, the rising expense and declining supply of sulfur may eventually eliminate the existing prohibitions for these conventional processes. The Iowa State University thermal decomposition process may overcome this problem through the use of inexpensive, high sulfur coal as the fuel source. Since this has never been tested, process development for the adaptation of the ISU process to phosphogypsum with high-sulfur coal will be necessary.

The lack of commercial incentives to encourage exploitation of the by-product phosphogypsum and the multiplier effect of the production paradox common to all wet process phosphoric acid production represent a major challenge to Florida acid producers. The magnitude of this challenge is demonstrated by simple arithmetic. The combined annual production capacity of Florida phosphoric acid plants currently approaches 6 million tons of P₂O₅. When operating at full capacity, those plants generate 30 million tons of phosphogypsum annually. That volume is added each year to an existing waste gypsum stockpile currently estimated at roughly 300 million tons. Adding that annual value of phosphogypsum on a continuous basis will triple the volume of waste gypsum stored in Florida by the year 2000. This trend is not likely to be reversed until the commercial exploitation of by-product phosphogypsum is feasible.

Reducing the state's gypsum disposal requirements was assigned a high priority when the state legislature created the Florida Institute of Phosphate Research to pursue solutions to phosphate-related problems. In June of 1980, Zellars-Williams, Inc. received a FIPR grant to identify existing processes for the exploitation of by-product gypsum, to isolate promising processes, to evaluate the technical and economic feasibility of adopting various potentially promising processes to the commercial exploitation of by-product phosphogypsum and complete a bench or pilot scale demonstration of the most viable process.

METHODOLOGY

The proposal submitted by ZW initially included a literature search, process evaluation and a preliminary technical/economic engineering study. The proposal also included a bench scale demonstration of the most promising process. The results of that demonstration were evaluated to isolate process modifications that might improve the technical or economic feasibility of the process. The conclusions resulting from that evaluation were then summarized and served as the basis for recommendations for additional research.

Literature Search

The literature search began with a thorough review of a 186-page bibliography provided by FIPR Director, Dr. David P. Borris. The bibliography summarized appropriate articles, presentations, theses, patents and symposiums through 1976. The bibliography was divided into four subject categories - Chemical Pathways, Construction Uses, Agricultural Application and Miscellaneous Applications - which were retained for the remainder of the study. The initial bibliography consisted of 608 abstracts, 30 percent on chemical applications, 36 percent on construction, 26 percent on agricultural applications and 8 percent on miscellaneous applications.

The original bibliography was supplemented by computer-assisted literature searches covering the period from 1977 to the present. A search of documents indexed by the American Chemical Society Abstract and the National Technical Information Service provided an additional 191 abstracts. Approximately 58 percent of the additional abstracts were originally published in the Soviet Union or its East European satellites. A final search of the Engineering Index and U.S. patent files provided another 86 abstracts.

The Literature search identified almost 900 abstracts, each of which was assigned to one of the four subject categories. The second stage of the literature search concentrated on reducing the number of abstracts actually selected for review. Several criteria were established to screen all 900 abstracts and select the most appropriate. Soviet-bloc abstracts were eliminated due to the lack of availability and expense of translation services and because of the questionable nature of the data. The remaining abstracts were then screened to eliminate duplication. A final screening step isolated individual abstracts within each subject category that concentrated on existing conceptual, experimental or commercial processes capable of converting waste gypsum into intermediate and final products of potential commercial value to Florida acid producers.

Of the almost 900 abstracts generated by the literature search, 15 or 20 percent were ordered for review. Both the literature search and abstract acquisition phases were conducted through FIPR. Approximately 10 percent of the abstracts were foreign p&tents which required translation. Upon arrival, each abstract was classified by subject and distributed for review and summarization. Individual summaries describe the data available in each abstract, list additional references and adequately index these references to facilitate rapid data retrieval.

The summaries were then subjected to a technical grading procedure to isolate specific processes worthy of additional evaluation. Both the quantity and quality of the data available in each abstract were graded. The criteria used to measure the abstracts were:

- Availability of sufficient data to establish process feasibility;
- Uses of and demand for the intermediate or final products resulting from the process;
- Potential reductions in gypsum disposal requirements;
- Marketing and distribution potential;
- Level of development (conceptual, bench scale, commercial);
- Length of bench or commercial operation;
- Economic feasibility; and
- Technical feasibility of equipment design and sizing to scale up for phosphogypsum applications.

The score for each criteria varied from zero to three yielding a maximum score for each abstract of 24 points. Abstracts scoring 14 or more points were retained. In addition, several abstracts which contained pertinent data but failed to score 14 points were filed for future reference. A complete bibliography of these articles which were referenced is included in this report. Rejected articles were returned to the FIPR library and are not included in the bibliography.

This final screening step in the literature search isolated references which contained a sufficient amount of data to facilitate technical and economic analysis of the processes described, particularly those processes which resulted in intermediate or finished products with potential commercial appeal. The selected references were then subjected to preliminary technical and economic engineering analysis.

Technical and Economic Evaluation

The retained references supplied the necessary data to establish preliminary process flowsheets for each viable process. The flowsheets assumed the process under evaluation operated in conjunction with an adjacent, 1,000 ton-per-day P₂O₅ wet process phosphoric acid plant. Mass and energy balances were calculated and used for preliminary equipment sizing and verification of the technical feasibility of the process.

Both capital and operating costs were estimated in evaluating economic feasibility. Capital costs were calculated from equipment quotes obtained through the appropriate vendors. Standard engineering cost estimation methods were used to calculate other capital costs. Operating costs were based on current utility and manpower costs and previously published unit consumption rates adjusted to the specified design basis. A variety of standard engineering methods were employed to determine the unit costs resulting from the estimated capital and operating costs.

Several of the processes subjected to engineering analysis proved impractical. Others were technically feasible but would utilize such small quantities of phosphogypsum or appeal to such limited markets that implementation in Florida was possible but not practical. Although the remaining

processes were technically feasible and consumed acceptable volumes of waste gypsum, none proved economically feasible -under prevailing economic conditions. However, some of the remaining processes were sufficiently flexible to warrant an analysis of available process modifications that might improve overall economic feasibility.

The modifications applied to an experimental thermal decomposition process developed at Iowa State University (ISU) proved particularly promising and a bench-scale demonstration of the process using existing equipment and facilities at ISU was undertaken.

Demonstration

Representative samples of Florida phosphogypsum were collected by ZW technicians and subjected to varying degrees of washing, drying and screening. Samples collected after each gypsum preparation technique were forwarded to the ZW analytical laboratory for chemical analysis in order to evaluate the success of the preparation steps. After an appropriate pretreatment method was chosen, a sufficient volume of phosphogypsum was prepared and shipped to ISU for pilot scale testing conducted August 25, 1981. The results of the demonstration were recorded and used for later experimental evaluation.

LITERATURE SEARCH AND EVALUATION

Agricultural

C. L. Lindeken and D. G. Coles¹ reviewed the radiological effects of phosphogypsum applications on radium contents of vegetables and concluded there is little basis for concern regarding a radiological hazard from this source.

Concerning fluorine contamination, R. Chhabra, et al.² studied the fluorine solubility relations of sodic soils treated with gypsum. Large amounts of by-product gypsum are scheduled for utilization in reclaiming a large (2.5 million ha) area of the Indo-Gangetic plains of India. The article concludes that the addition of gypsum reduces the levels of plant available fluorine, with moderate amounts of fluorine in the gypsum not affecting this result.

J. A. Daughtry and F. R. Cox³ compared the effects of gypsum versus phosphogypsum on Ca availability and concluded that there was no appreciable difference among sources.

From the above, it appears that phosphogypsum is comparable with other gypsum for 1st application, and poses no contaminant threat.

C. A. Anderson and F. G. Martin⁴ conducted a soil pH-added calcium experiment to determine the effects of these on the growth of young citrus trees. Their results indicate that agricultural limestone is superior to gypsum for citrus because limestone increases soil pH and has a much greater residual effect. However, G. A. Sullivan et al.⁵ studied interactive effects of dolomitic limestone, gypsum, and potassium on peanuts, and demonstrated the superiority of gypsum as a calcium source for peanuts. Sullivan also indicated that potassium is less detrimental to yield and quality of peanuts when applied in combination with gypsum. Daughtry and Cox³ also reported improvement in peanut crops with gypsum applications.

Several studies demonstrate that sulfur applications can have beneficial effects on agricultural yields. T. W. Walker⁶ indicated sulfur applied as gypsum improved forage yields, particularly by increasing the growth of clover and thus raising the rate of nitrogen fixation. In his work, he concludes that gypsum yields better initial and residual responses than elemental sulfur when applied at similar rates.

J. E. Matocha⁷ also studied the effects of sulfur source on forage yields of coastal Bermudagrass (Cynodon dactylon (L.) Pers). His results indicate 50 kg. S/ha as gypsum are at least as effective as 200 kg/ha sulfur applied as prilled elemental sulfur. He did note increased response to elemental sulfur the second year. The data also showed a significant S x Mg on forage yields the second year after gypsum application.

J. D. Beaton et al.⁸ evaluated several sulfur sources for alfalfa and concluded that gypsum provided more beneficial results than sulfur-gypsum, elemental sulfur, and ammonium phosphate plus sulfur. They suggest that in a dry climate a single application of gypsum would prove beneficial for a number of years, but feel that in a wetter climate residual benefits would decline as the sulfate leached out.

This leaching effect is also noted by A.F.R. Adams⁹. He indicates that gypsum applied at not less than 22 kg/ha. sulfur is the most effective form for adding sulfur to pastures in the first year. Elemental sulfur at 88 kg/ha gives a residual effect for a number of years, whereas gypsum required yearly applications for sustained yields. Apparently, the high rainfall (46 in./yr.) rapidly leached the sulfate.

C. During and M. Cooper¹⁰ dealt with this problem in a soil with high sulfate retention by using a single application of 168 kg/ha sulfur as gypsum, which they state protected the pasture against all but a slight deficiency of sulfur for 5 years, the total span of the experiment. Yields were the same as four annual applications of 45 kg/ha each. They note, incidentally, a higher survival of white clover in a dry summer under high rates of gypsum addition.

K. N. Bansal and H. G. Singh¹¹ studied the interactions of sulfur and iron in reducing chlorosis of cowpeas (Vigna sinensis End. Ex. Hassk). Their results indicated that soil treatments with iron sulfate or gypsum were only 82 percent as effective as elemental sulfur in reducing chlorosis caused by sulfur deficiency. They did show benefits from gypsum, however, as yields were increased. Their results do indicate that apparent micro nutrient deficiencies may be caused by sulfur deficiencies, although the authors recommend foliar applications of H_2SO_4 to correct them.

Vinod Kumar and M. Singh¹² researched soybean (Glycine max (L.) Merrill) response to sulfur, phosphorus, and molybdenum, but did not use gypsum as a sulfur source. They showed moderate levels of sulfur application (up to 80 ppm in soil) tend to increase soybean yields, whereas high levels (120 ppm in soil) decreased yields.

J. R. Davis et. al.¹³ studied the effects of various materials in controlling potato scab. They indicate gypsum or sulfur at 600 pounds/ac effectively control scab (loss reduction of 53 percent), but were not effective at lower rates. Since neither material lowered the soil pH significantly (0.1 to 0.4 units), the authors felt this was not the controlling factor. Their research was conducted in a highly buffered calcareous soil.

The literature evaluation indicates that gypsum can be of value as a sulfur source for various crops, particularly legumes. Quantities required vary depending on crop, local climate; and soil characteristics.

Gypsum has a high utility for reclamation of saline and alkali soils, and some use in lateritic soils. K. Dale Ritchey et. al.¹⁴ demonstrated an increase in rooting depth and drought resistance in corn (Zea mays L.) in a Brazilian Savannah soil after calcium leaching with gypsum. They indicate beneficial effects from a reduction of the aluminum to base ratio; increased availability of Ca in the subsoil, and an increase in pH. However, they also indicate a loss of K and Mg in the surface soil due to increased leaching.

The effects of gypsum applications on an Australian sandy loam soil- were studied by B. J. Bridge and C. R. Kleiniga¹⁵. They applied 10 metric tons/ha to test plots. Higher water contents in the soil profile both before and after irrigation were attributed to increased hydraulic conductivity and porosity in the subsoil as a result of the gypsum treatment.

The chemistry of sodic soil reclamation with gypsum and lime is outlined by J. O. Oster and H. Frenke¹⁶, who model the kinetics of the process and simulate the actions of the various ions involved to predict the amounts of gypsum required for various desired levels of reduction in exchangeable sodium percentage. They confirm their model with experimental data from the U.S.D.A. Salinity Laboratory Staff¹⁷ and others. T. K. Glas et al¹⁸ performed experiments on the rates of dissolution and transport of gypsum in soils. The results were compared with several models in an attempt to determine controlling factors. Of more importance is the author's note of non-systematic variations of up to 30 percent in recovered gypsum mass for natural gypsum, which was not observed with reagent grade gypsum. This is attributed to irregularities in the natural material.

G. R. Dutt et al¹⁹ also predict gypsum requirements for maintenance of optimal water infiltration rates when sodic soils are leached. The predictions are modeled on several factors. Experimental work performed by the authors seems to confirm the predicted effects. The inclusion of irrigation quality water in the model seems to be of some utility in areas where the dissolved salts content varies.

The method of gypsum placement in the soil was studied by I. P. Abrol et al²⁰. They indicate gypsum requirements are reduced by half when the application is made onto the soil surface instead of mixing the gypsum throughout the soil. They also indicate that some previous methods for determining gypsum requirements neglected soluble carbonates in the soil and thus overestimated gypsum requirements. However, they did not seem to be aware of the work of the previous authors.

Later experimental work by Abrol and D. R. Bhumbra²¹ used differential rates of application with several different crops. Their results show differential responses according to the crop and seem to indicate the need to tailor the gypsum quantities used to the crop being grown. However, yields were dramatically increased for several crops, indicating that benefits may be realized from gypsum.

U. C. Shukla and A. K. Mukhi²² studied nutrient interactions on alkali soils treated with gypsum. and state that the ameliorative effects of gypsum may be due not only to the improvement in soil structure, but also to the increase in nutrient availability.

The size of gypsum particles used for soil upgrading may influence the effectiveness of treatments. R. Keren et al²³ indicate that large amounts of fine gypsum (L44 um) may actually reduce hydraulic conductivity rather than increase it. This effect is attributed to a clogging of pore space.

B. J. Alawi et al²⁴ indicate that, in Arizona soils, sulfuric acid may be the preferred reclamation material for preventing soil dispersion during leaching. They studied the effects of both H_2SO_4 and gypsum amendments on soil properties and sudangrass yields. They conclude that for their region, applications of sulfuric acid are more effective and more cost effective than gypsum because the acid is available as a processing by-product and provided the equivalent of two growing seasons. The soils studied did contain sufficient calcium to prevent dispersion of the soils under leaching, which is always the case.

Gypsum is valuable in reclamation of saline and alkali soils, and upgrading of lateritic soils. Although requirements may vary, quantities are generally much larger than those required for fertilizer purposes. However, this is often a one-time use and is most beneficial in those soils which would become dispersed under leaching.

Transportation costs for shipping phosphogypsum and the cost/benefit ratio for application are the two primary economic considerations for agricultural use of phosphogypsum.

As a competitor of limestone or dolomitic limestone, gypsum is normally preferred only with peanuts. For most other crops, the residual calcium supply and the lower cost per acre make limestone the preferred soil amendment. In addition, limestone and dolomite raise the pH of the soil, which is often recommended in acid soil areas. The rapid availability of the calcium in gypsum, however, has prompted its use for peanuts. The gypsum application is made at the time of flowering, thus the higher solubility of gypsum appears to yield increased levels of available calcium at the critical period for this crop.

In 1979, the U.S. planted acreage in peanuts was steady at 1.5 million acres²⁵. At an average application rate of about 450 lbs/acre²⁶ about one-third of a million tons of gypsum would be required annually.

For crops other than peanuts, gypsum would need to be available at \$10 a ton to compete with agricultural lime at \$17 a ton, on a cost per hundred weight calcium basis.

Personal communications with several fertilizer salesmen indicate that in the Polk County region, hauling charges for phosphogypsum would be about \$15 a ton. If this cost could be reduced and the at-plant material cost was sufficiently low, phosphogypsum might be cost-competitive with agricultural lime.

As a sulfur source, gypsum is much more competitive with other available sources. At \$300 per ton of elemental sulfur, gypsum at \$55 a ton is about equivalent on a cost per hundred weight sulfur basis. In addition, the sulfur in gypsum is more rapidly available. This effect is beneficial for sulfur deficient soils, but also decreases the residual availability of sulfur, particularly in regions with high rainfall levels.

Legumes have shown a particularly positive response to sulfur amendments. However, in many regions of the U.S., atmospheric contributions of sulfur are of a magnitude necessary to replace any loss to crops. For sulfur deficient soils, about 800 lbs/acre of gypsum has been recommended for soybeans in India¹². If the same rate was used in the U.S. on all soybean acreage, about 10 million tons/year would be required. However, not all soils are sulfur deficient, and in many regions sulfuric acid is available as a minerals processing by-product at low cost. For these reasons, it is not expected that any great increase in the use of phosphogypsum as a sulfur source can be anticipated.

The price competition between gypsum and sulfuric acid also has bearing on the land reclamation aspects of gypsum application. However, the use of sulfuric acid for reclamation of alkali and saline soils requires calcium in the soil to prevent dispersion. Thus, in many regions, gypsum is still the preferred material.

Application rates of gypsum for reclamation of saline and alkali soils are much higher than those for fertilizer use. Recommended rates are on the order of 10 tons/acre. However, these are often one-time applications. Even in areas with slightly saline irrigation water, one treatment about every four years is typical.

Thus in India where there is an estimated 2.5 million hectare area of salt-affected soils², about 40 million tons of gypsum would be required annually on a four-year application cycle, or about 160 million tons for a one-time application.

Construction

A number of articles were obtained that fell into the building industry. Abstracts in the construction category concentrated on processes utilizing phosphogypsum to produce plaster, wallboard, plaster products and building blocks. In these cases, the purification of phosphogypsum and not sulfur value recovery was the major concern.

The process of major interest in this category is the CdF Chemie process for phosphogypsum purification. This process was described in detail in several articles^{27, 28} and was further investigated through personal contact. This process is currently in full-scale operation in France and involves a succession of counter current washing, filtering and flash drying steps to produce a hemihydrate product suitable for production of wallboard and building materials. The design and operation of this type of plant seems feasible as a method of cleaning the phosphogypsum and supplying a raw material to local wallboard and building material producers. Details of this process are included in the preliminary engineering and economics section.

A process which produces a versatile building material called masan was investigated but never specifically defined due to lack of information. The Maes²⁹ process was developed by a Belgian engineering firm and was scheduled for full-scale operation in Ostende, Belgium in 1976. The process consists of four basic steps: dewatering, calcination, cooling, and crushing. The product can be converted into conventional cement, water-resistant cement and prefabricated building materials using special binders developed for each specific application. The data was insufficient for preliminary engineering evaluation and subsequent attempts to locate additional information failed. The area where this type of plant was located must generate a sizable demand for building products to ensure a large consumption of phosphogypsum.

In other areas where natural gypsum is unavailable, processes have been developed to utilize phosphogypsum. An article written about the Imperial Chemical Industries, Inc. (ICI) process utilized phosphogypsum to produce a stucco product suitable for plasters and plasterboard fabrication. The process

is a standard, dry-phase dehydration method consisting of converting phosphogypsum to beta-hemihydrate through purifying the gypsum by slurring and filtering before drying and calcining in two separate steps. The two full-scale plants in operation in 1966 ceased production in 1968. The process was extremely vulnerable to fluctuations in the impurities found in phosphogypsum and the plants were phased out due to operating difficulties.

In later years, ICI developed another process to convert phosphogypsum to alpha-hemihydrate by wet phase dehydration. The ICI Alpha hemihydrate process described by Allen³¹ produces a purer calcium sulfate product and operates on a continuous basis, unlike the old process. The new process involves slurring the phosphogypsum, adding crystal habit modifiers, adjusting pH, and pumping to high pressure autoclaves where the phosphogypsum is rapidly converted to the alpha-hemihydrate. The hemihydrate can either be dried into plaster or reslurried and used for gypsum blocks. One advantage to this process is that the raw feed does not require washing unless it is grossly contaminated. The existing plant has a capacity of 15 short tons/hour hemihydrate or a phosphogypsum consumption rate of only 18.3 short tons/hour. The plant could be upgraded but would require a tremendous market for plaster products and gypsum blocks.

A similar process described in another article,³² the Giulini process, converts phosphogypsum into alpha-hemihydrate used for molding blocks. The process begins with a series of flotation steps to remove impurities before autoclaving at 110° to 120°C and 1 atmosphere pressure to yield the alpha-hemihydrate. An operating plant in West Germany has a capacity of only 150 tonnes per day (tpd) and the phosphogypsum consumption is very low. To construct a plant to consume even one-half of the phosphogypsum produced in a standard phosphoric acid plant (1000 tpd P₂O₅) would require a tremendous demand for these low density blocks. No such demand presently exists in Florida.

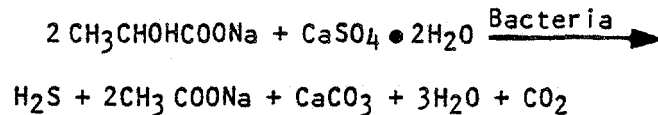
The production of alpha-hemihydrate represents a relatively small percentage of the plaster/building materials industry utilizing phosphogypsum. The majority of the plaster products are made from beta-hemihydrate, which is produced by the dry phase dehydration process. One example of this method is the Rhone Poulenc process. This process is in full-scale operation in Rouen, France and is capable of producing 250,000 mtpa of hemihydrate (a consumption of approximately 375,000 metric tons of phosphogypsum). Variations in the Rhone Poulenc process have been developed and are used depending on the nature of the phosphogypsum. Two alternates were described in an article²⁸ covering existing beta processes in Europe. The dry-phase process is much more susceptible to variations in impurities in the feed stock and the cleaning/washing stages of the process must be consistent for proper process control. Cleaning can be performed by either flotation or cycloning and the drying stage can occur in either a one step drying/calcination process in a fluid bed or two distinct drying and calcination units. The variations are used depending on the type of phosphogypsum and plant location. This process has been licensed in several other foreign countries (Brazil, Rumania) and plants of varying capacities have been constructed. The economic incentive of this process is the lack of inexpensive natural gypsum. In areas where gypsum is readily available, the increased operating cost of cleaning stages rules out the use of phosphogypsum. If a cleaning method for by-product gypsum can be designed or altered to provide a clean product that can then be transported to gypsum users for the same cost or less, substituting by-product gypsum may prove feasible.

Several other plaster processes²⁸ were reviewed but not detailed due to either lack of information or similarity to the CdF Chemie process. Such processes as the Knauf phosphogypsum processes (S1-S111), the Cerphos process, the FCI process, and the Allied Chemical process are all variations of the dry phase dehydration conversion process.

Miscellaneous

This category includes abstracts which did not pertain specifically to one of the three major categories. A substantial number of articles were classified in this category due to the variation in material presented.

One of the most intriguing topics included in the miscellaneous section was microbiological reduction of gypsum. This procedure was described by Corrick, et al³³ in research for the Bureau of Mines. The initial work was in anaerobic fermentors, with emphasis on defining the optimum pH, temperature, bacteria number and maximum hydrogen sulfide production. Two types of anaerobic bacteria were tested, both yielding the following typical reaction:



The optimum production rate was 7.13 g H₂S/Liter of fermenter volume in a medium of 60 percent sodium lactate solution. One other medium which performed as efficiently as the sodium lactate solution was buffered, polymerized whey. Both natural and by-product gypsum can be reduced in this manner; however, due to the type of biological medium required and the high fermentor exchange rate (70% of volume in a 24-hour period), this procedure is not economically feasible in a large scale system.

A later article³⁴ discusses bench-scale work on microbiological reduction of gypsum with *Desulforibrio desulfuricans* to hydrogen sulfide in the presence of various carbon sources. The authors theorize that the hydrogen sulfide can be converted to sulfur by limited oxidation using cultures of *Chlorobium* and *Chromatium*. This would provide a microbiological system for complete conversion to sulfur. The production rates discovered in the bench-scale work were low but could be increased by using actively multiplying cells. Another attractive idea is the use of organic waste products such as sewage and spent distillery liquor as the hydrogen source instead of the expensive organic mediums used in the bench-scale work. This work is still in the preliminary stages, no design consideration was attempted. However, this process could become economically attractive if further studies prove that inexpensive waste materials and rapid multiplying sulfate reducing bacteria could be utilized.

Other work in this category applied gypsum as roadbed and a variety of other small-scale uses. It was decided not to pursue this type of approach as the purpose of this study was to locate an attractive method for disposing of the phosphogypsum on a large-scale basis.

Chemical Processing

The majority of chemical abstracts dealt with some type of thermal decomposition yielding CaS, H₂S, S₀2 or elemental sulfur as the main product. The disadvantage of these processes is the intense energy requirement, which is not economically feasible due to current high fuel costs. However, this can be mitigated with the use of inexpensive high sulfur fuels, as is the case with the ISU process.

The ISU process was developed from original work with anhydrite conducted by Wheelock and Boylan³⁵ at Iowa State University. The process involves thermal decomposition of CaSO₄ into lime and S₀2 gas in a two-zone fluid bed reactor. There are several patents on this development work,^{36,37,38,39} all of which were referenced for the preliminary engineering design and economics analysis. Alterations to the original process are discussed in detail in the preliminary engineering and economics section of this report and were made with the review and approval of the inventor.

Several groups have worked on similar processes. Campbell, et al, have several patents on a thermal decomposition process which utilizes natural gypsum or anhydrite. One patent⁴⁰ describes the decomposition of CaSO₄ to S₀2 gas and a metal sulfide that is subsequently oxidized to a metal oxide in an oxidation chamber. They state that a very pure solid product may be obtained by carrying the initial solid product through alternating reduction and oxidation zones. A later patent⁴¹ describes a process where gypsum is contacted with reducing gases to yield S₀2, CaO, and CaS. The metal sulfide may subsequently be converted to H₂S and sulfur in a second reducing reactor, producing a sulfur product in various forms. These two similar processes were rejected because the ISU process combines reduction/oxidation in one reactor step to produce the same products.

Several processes utilizing phosphogypsum in the manufacture of ammonium phosphate fertilizers were reviewed. One patent⁴² describes a process where phosphogypsum is reacted with ammonium carbonate (or ammonia and CO₂) to produce ammonium sulfate. The ammonium sulfate is then contacted with a hydrogen ion exchange resin which produces sulfuric acid. Phosphoric acid is then produced from this sulfuric acid and phosphate rock. The phosphoric acid is then contacted with the ion exchange resin to regenerate it and form ammonium phosphates. Another article by Meline, et al⁴³ discusses a pilot-scale fertilizer process using nitric acid for acidulation and phosphogypsum as a possible sulfate make-up source. The process produces a by-product calcium carbonate and a 28-14-0 fertilizer product. Both processes provide methods of fertilizer production where the phosphogypsum problem is not inherent; however, the products are not standard grade for the Florida producers and there would be considerable justification required to convert to one of these processes. Conversion is not currently justified.

Several articles and a patent involving the production of ammonium sulfate were reviewed. One Japanese article⁴⁴ gave experimental data and a brief description utilizing by-product gypsum and ammonium carbonate, but no further information was included and additional attempts to locate the unabridged article were unsuccessful. Another article⁴⁵ described a simplified ammonium sulfate process developed by Continental Engineering of the Netherlands. This

process introduced slurried gypsum in a tall cylindrical reaction vessel with ammonia and CO_2 . The reacted slurry is filtered via a rotary drum filter, producing the ammonium sulfate from the calcium carbonate filter cake and recycling the filtrate to the slurry tank. The simplification reduces capital expenditures and lowers operating cost somewhat more than the standard ammonium sulfate process. Another article⁴⁶ discusses the production of ammonium sulfate from natural gypsum and its full-scale development in Germany and Britain. Even at the time the article was written (1957), such a process was not feasible in the U.S. and is less feasible today due to the low market for ammonium sulfate.

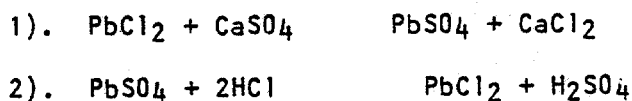
Another process evaluated in the preliminary engineering and economics section is the OSW-Krupp process. Several articles^{47,48,49} received describe the process in detail and all were used to some extent. In this process, phosphogypsum is substituted for anhydrite and is thermally decomposed with proper additives to form cement clinker and SO_2 . The process is in full-scale operation in Phalabora, South Africa and has a capacity of 350 tpd cement clinker and sulfuric acid. From its early design, the process has been upgraded and altered to improve energy efficiency. The process is presently feasible only in areas where there is a large demand for cement and no accessible sulfur source. Depending on the price of sulfur, this process could become a reality in the Florida area with proper backing and distribution of the cement clinker product. One possibility is a fertilizer company with subsidiaries or interests in the cement industry to market the quantity of cement clinker produced.

A similar process that is also in full-scale operation is the Marchon process, which produces SO_2 and port land cement. Articles^{50,51} with specific details on the full-scale operations were reviewed and evaluated. This process is very similar to the OSW-Krupp process and was an attempt to use abundant local anhydrite to replace non-existent elemental sulfur.

Both the Marchon and OSW-Krupp processes are merely modifications of the original Mueller Kuhne⁴⁹ process for the production of portland cement and SO_2 from gypsum. This process adds carbon to the kiln feed, along with the proper mix for a cement product, to lower the temperature requirement for the reaction. Due to the fluctuations in market prices for sulfur, the operating plant was converted to burn sulfur in 1975. Because of the difficulties in meeting U.S. portland cement specifications and the economic necessity of selling all the by-product cement, this process currently seems impractical in the Central Florida area. It was not investigated in the Engineering section due to the similarity to the OSW-Krupp process.

Bench scale work was reported in several articles^{52,53} on a process involving electrolysis of a sodium chloride-phosphogypsum mixture yielding an SO_2 gas and a calcium sulfide-calcium oxide mixture with a 40 percent SO_2 recovery. Due to the low recovery and impure solids product, this process was also not evaluated. Additional research would be necessary to determine if the process could ever be economically feasible.

An Indian process described by Kappanna⁵⁴ utilizes lead chloride, gypsum and hydrochloric acid to produce sulfuric acid on a pilot scale level. The reaction goes as follows:



The lead chloride is recycled; however, it would be difficult to maintain process control in a large scale plant to prevent lead contamination of the CaCl_2 product. Due to the hydrogen chloride consumption, this would be feasible only where hydrochloric acid is abundant. The potential for environmental problems with systems using lead on a large scale would outweigh the environmental improvement of disposing of the phosphogypsum.

Many other articles were reviewed and some contained valuable information which did not pertain to any specific application. Where applicable, these articles have been referenced.

Summary

The literature evaluation indicates a variety of commercial applications of phosphogypsum are potentially feasible. However, the agricultural and miscellaneous applications would consume only a small portion of the phosphogypsum produced in Florida. The chemical processing category appears to be the only one capable of consuming large quantities of phosphogypsum for commercial exploitation with the construction industry being the next category. The CdF Chemie process was evaluated as it could be put into application by one of the smaller acid producers to provide raw material to gypsum plants in the Florida area. The two most promising chemical processes were also subjected to an analysis of their technical and economic feasibility for Florida phosphogypsum. The processes are: the ISU process and the OSW-Krupp process.

TECHNICAL AND ENGINEERING ANALYSIS

OSW-Krupp Process

A preliminary engineering study and economic analysis of the OSW-Krupp process to convert phosphogypsum to portland cement and SO₂ was completed.

The fixed capital cost for addition of this process (battery limits only) to an existing 1,000 TPD P₂O₅ facility was estimated at \$40.6 million (see Table I). This does not include the cost of a sulfuric acid-plant or gypsum feed preparation such as washing or sizing.

The operating costs were estimated on the basis of using low sulfur no. 6 fuel oil only, as this process has not operated with high sulfur fuels (see Table II). 47,49,55,56

The operating costs for the OSW-Krupp process are shown for several different bases in Table III. Without taking a credit for the cement, the cost is \$263.74 per long ton sulfur equivalent; with a \$45 per ton of cement credit, the cost is \$112.15 per long ton sulfur equivalent. Based on a sulfur price of \$120 per long ton, the return on investment after taxes is 7.7 percent, with the cement credit.

Table I
OSW-Krupp Process
Fixed Capital Cost

Total Installed Equipment	\$28,400,000
Sales Tax	920,000
Labor Fringes	<u>1,180,000</u>
Total Direct Cost	\$30,500,000
Field Distribution	3,050,000
Engineering	<u>3,350,000</u>
Total Direct and Indirect Cost	\$36,900,000
Contingency	<u>\$ 3,700,000</u>
Total Fixed Capital Cost	<u><u>\$40,600,000</u></u>

Process Description

Phosphogypsum is fed to a rotary dryer where the surface moisture and water of crystallization are removed (see Figure 2). The rotary dryer is vented to a baghouse where dust is removed prior to venting. The dried gypsum, now anhydrite, is conveyed by bucket elevator to storage silos. The additives, coke, sand, and clay are dried in the additive dryer, then conveyed by bucket elevator and belt conveyor to their respective storage silos.

Table II
OSW-Krupp Process Operating Cost

	Amount/Ton H ₂ SO ₄ or Cement	Cost/Unit of Input	Cost/Ton of H ₂ SO ₄ or Cement
1.) Raw Materials			
a.) Phosphogypsum	1.75 Ton	\$ -0-	\$ -0-
b.) Clay	0.07 Ton	6.00	0.42
c.) Sand	0.07 Ton	10.00	0.70
d.) Coke	0.10 Ton	55.00	5.50
e.) Gypsum (add to cement)	0.04 Ton	-0-	-0-
2.) Utilities			
a.) Electric Power	141 KWH	0.045	6.35
b.) Cooling Water	.250 MGAL	0.04	0.01
c.) Fuel (Low Sulfur #6 Oil)	9.45 MMBTU	5.10	48.20
3.) Labor			
a.) Operating Labor	0.17 MHR	7.00	1.19
b.) Supervisory (40% of operating labor)			0.48
4.) Maintenance (5% of fixed capital/year)			3.03
5.) Indirect Costs			
a.) Depreciation (15 year straight-line)			
b.) Taxes and Insurance (2% fixed capital/year)			1.21
c.) Plant Overhead (60% of labor cost)			1.00
6.) Loss of Steam Credit	2 MMBTU	5.10	<u>10.20</u>
Total Cost			<u>\$ 78.29</u>
Credit for by-product Cement	1 Ton	45.00	<u>45.00</u>
Net Cost			<u><u>\$ 33.29</u></u>

Table III
OSW-Krupp Process Operating Cost Comparison

Total Operating Cost * for Low Sulfur #6 Oil (\$5.10/MMBTU)

A. Without credit for by-product cement

\$ 78.29 per ton H₂SO₄ produced
\$263.74 per long ton sulfur equivalent
\$ 42.48 per ton gypsum processed
\$156.58 per ton P₂O₅ produced

Percent return on investment after taxes = -14.0%

B. With credit of \$45.00 per ton for by-product cement

\$ 33.29 per ton H₂SO₄ produced
\$112.15 per long ton sulfur equivalent
\$ 18.06 per ton gypsum processed
\$ 66.52 per ton P₂O₅ produced

Percent return on investment after taxes = 7.7%

* All operating costs in gypsum disposal and conversion areas only. Does include loss of steam credit from substituting gypsum for liquid sulfur. Includes 15 year straight-line depreciation.

Note: Does not include cost of sulfuric acid plant.

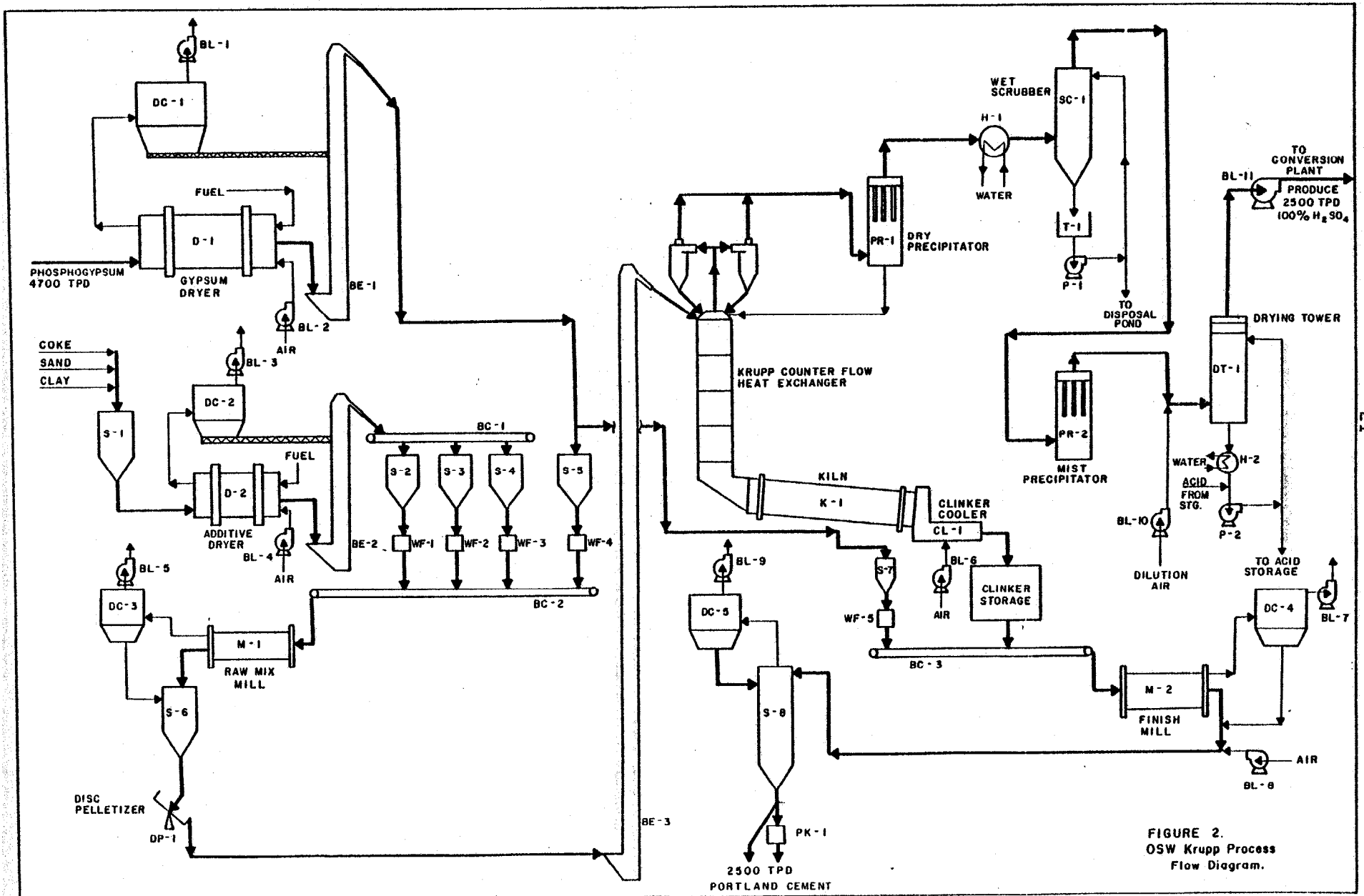


FIGURE 2.
OSW Krupp Process
Flow Diagram.

The anhydrite and additives are metered by weigh feeders onto a belt conveyor which feeds the raw mix mill which grinds and mixes the material. The ground raw mix is stored in a silo prior to pelletization. The pelletized raw mix is then fed by bucket elevator to the top of the Krupp kiln preheater.

The SO₂ and clinker are formed in the rotary kiln. The SO₂ exits the kiln through the preheater and cyclones. The dust-laden offgas is passed through a dry precipitator, then through a water cooler. The cooled gas is further cleaned in a wet scrubber. The gas then goes through a mist precipitator to remove the impure acid formed at that point. After dilution with air to the proper oxygen content for the acid conversion plant, the gas is dried in a tower by passing concentrated H₂SO₄ through the gas stream. The dried, clean gas is then blown to the acid conversion plant.^{47,48,49,55,56,57}

The clinker exits the kiln through a stoker cooler and is then piled in the clinker storage area to cool. The cooled clinker and gypsum are metered onto a belt conveyor feeding the finished cement mill. The finished cement is air conveyed to the finished product silos. The portland cement product can be shipped either in bulk or bags.

Preliminary Capital and Operating Cost Estimates

This capital cost estimate includes only the fixed capital costs of the battery limits plant shown on the flow diagram, Figure 2. Neither the sulfuric acid plant capital cost nor the gypsum feed preparation costs, such as washing or sizing, are included. (See Table I)

The fixed capital cost was developed on the basis of an addition to an existing facility. Working capital and offsites were not included. The equipment and motor lists used in the capital cost estimate are contained in the appendix.

These operating costs were estimated using low sulfur #6 fuel oil, as no data was available concerning the possibility of using high-sulfur fuels. The existing facilities use low-sulfur fuel oil.^{47,48,49,55,56,57} These costs include the gypsum disposal and conversion areas only; they do not include costs in the sulfuric acid plant. However, they do include the loss of steam credit from substituting gypsum for liquid sulfur.

CdF Chemie Process

A preliminary engineering study and economic analysis completed for the CdF Chemie process to wash phosphogypsum and produce a stable, high-quality hemihydrate product.

The fixed capital cost for addition of this process (battery limits only) to an existing 1,000 TPD P₂O₅ facility was estimated at \$28.2 million (see Table IV).

The operating costs were estimated on the basis of using low sulfur no. 6 fuel oil only, as this process currently employs only low-sulfur fuels.^{27,28,58}

Table IV
CdF Chemie Fixed Capital Cost

Total Installed Equipment	\$19,900,000
Sales Tax	600,000
Labor Fringes	<u>700,000</u>
Total Direct Cost	\$21,200,000
Field Distribution	2,100,000
Engineering	<u>2,300,000</u>
Total Direct and Indirect Cost	\$25,600,000
Contingency	<u>2,600,000</u>
Total Fixed Capital Cost	<u><u>\$28,200,000</u></u>

The estimated operating costs for the CdF Chemie process are shown in Table V. The cost is \$11.15 per short ton of hemihydrate and \$8.71 per short ton of phosphogypsum processed. Based on a hemihydrate cost of \$25.28 per short ton, produced from natural gypsum and shown in Table VI., the return on investment after taxes is 33 percent.

Process Description

Phosphogypsum from the phosphoric acid plant is fed to an agitated tank where it is slurried with recycle water (see Figure 3).^{27,28,58} This slurry is then screened to remove the coarse phosphate rock and quartz, this oversize material being pumped to a disposal area. The underflow from the screening section is then reslurried in another wash tank. This material is hydrocycloned to dewater and remove the very fine impurities. The dewatered gypsum is then reslurried with fresh water for a final wash. This slurry is hydrocycloned and reslurried with recycle water in a tank, where a lime slurry is added to neutralize any remaining acid prior to filtration. The neutralized slurry is then filtered on horizontal belt filters with the filtrate being recycled to wash tanks.

The filter cake is fed to a flash dryer where the surface moisture is removed. The dry gypsum is then fed to another flash dryer where the 1½ molecules of water are removed to produce hemihydrate. At this point, a smaller portion is converted to anhydrite. The product of this flash dryer is fed to a third unit where the warm humid air from the first flash dryer is recycled allowing for re-hydration of the anhydrite to hemihydrate and crystal habit modification.

The product of this unit is the stable hemihydrate which can be used for wall board production or plaster. The dirty gases produced by the flash dryers are first cooled by pre-heating the combustion air and fuel oil, then the particulates are removed in a wet scrubber prior to being vented to the atmosphere.

Table V
CdF Chemie Process Operating Cost

	<u>Amount/Ton Hemihydrate</u>	<u>Cost/Unit of Input</u>	<u>\$/Ton of Hemihydrate</u>
1.) Raw Materials			
Phosphogypsum (dry basis)	1.28 Ton	-0-	-0-
2.) Utilities			
a.) Electric Power	29 KWH	\$ 0.045	\$ 1.31
b.) Fresh Water	2.0 MGAL	0.04	0.08
c.) Fuel - Low Sulfur #6 Oil	1.21 MMBTU	5.10	6.17
d.) Lime	15 LB	0.025	0.28
3.) Labor			
a.) Operating (2 men/shift + dayman)	0.015 MHR	7.00	0.11
b.) Supervisory & Analytical (40% of operating labor)			0.04
4.) Maintenance (5% of fixed capital/year)			1.12
5.) Indirect Costs			
a.) Depreciation (15 year straight-line)			1.50
b.) Taxes and Insurance (2% fixed capital/year)			0.45
c.) Plant Overhead (60% of labor cost)			<u>0.09</u>
Total Cost			<u><u>\$11.15</u></u>

Table VI
Standard Hemi-hydrate Operating Cost

	<u>Amount/Ton Hemihydrate</u>	<u>Cost/Unit of Input</u>	<u>\$/Ton of Hemihydrate</u>
1.) Raw Materials			
Natural Gypsum (dry basis)	1.5 Ton	11.50	17.25
2.) Utilities			
a.) Electric Power	19 KWH	\$ 0.045	\$ 0.86
b.) Fuel - Low Sulfur #6 Oil	0.95 MMBTU	5.10	4.84
3.) Labor			
a.) Operating (3 men/shift + dayman)	0.04 MHR	7.00	0.28
b.) Supervisory & Analytical (40% of operating labor)			0.11
4.) Maintenance (5% of fixed capital/year)			0.63
5.) Indirect Costs			
a.) Depreciation (15 year straight-line)			0.83
b.) Taxes and Insurance (2% fixed capital/year)			0.25
c.) Plant Overhead (60% of labor cost)			<u>0.23</u>
Total Cost			<u>\$25.28</u>

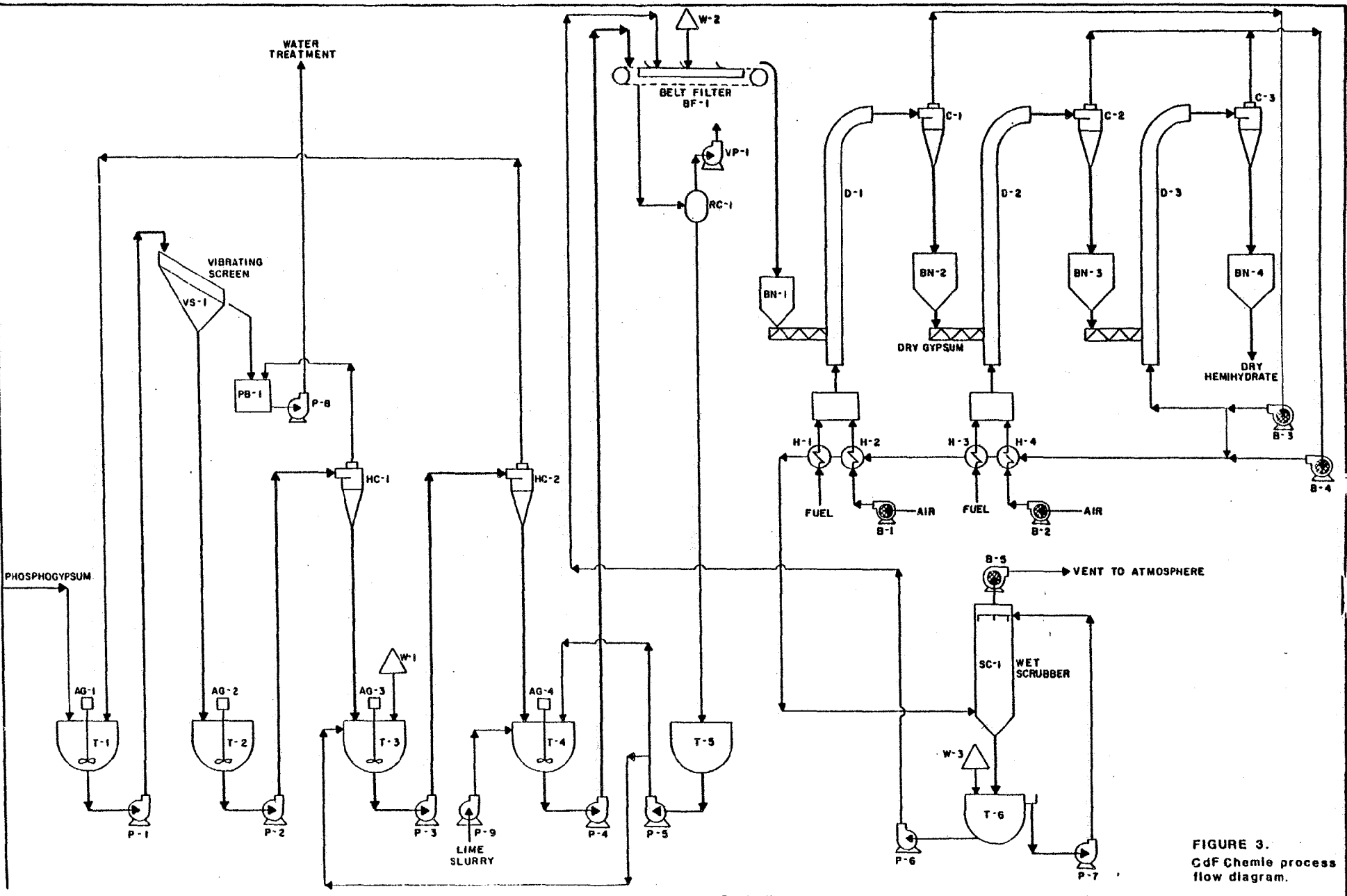


FIGURE 3.
CdF Chemie process
flow diagram.

ISU Process

A preliminary engineering study and economic analysis of the Iowa State University process to convert by-product phosphogypsum to quicklime and sulfur dioxide was completed.

The fixed capital cost for addition of this process (battery limits only) to an existing 1,000 TPD P₂O₅ facility was estimated at \$27.7 million (See Table VII). This does not include the cost of a sulfuric acid plant or gypsum feed preparation steps such as washing or sizing.

Operating costs were estimated on the basis of three alternate fuels: low sulfur number 6 fuel oil, high sulfur number 6 fuel oil, and high sulfur coal. Without taking any credit for the by-product lime, the operating costs were \$164.46, \$147.38, and \$105.17 per long ton sulfur equivalent, respectively. With \$40 per ton credit for the by-product lime, the operating costs were \$87.65, \$70.58, and \$28.36 per long ton sulfur equivalent, respectively. The effect of fuel cost on the operating costs is demonstrated by Figures 4 and 5.

The effect of sulfur equivalent cost on the after tax return-on-investment (% ROI) is shown on Figures 6 and 7. The percent ROI for low and high sulfur number 6 fuel oil and high sulfur coal, without taking any credit for the by-product lime, was -16.8 percent, -10.1 percent, and 5.7 percent, respectively. With a \$40 per ton credit for the lime the ROI was 12.1 percent, 18.6 percent, and 34.9 percent, respectively.

The price of \$40 per ton of by-product quicklime is conservative, as the current price for quicklime in the state of Florida is approximately \$50 per ton.

The economics of this process appear very favorable when high sulfur coal is used as a fuel. The 34.9 percent return on investment after taxes is almost double that of the next best fuel. However, as sulfur prices rise, the profitability of other fuels increases. The rate of increase of sulfur prices versus fuel prices will influence the final decision on which fuel to use.

The ISU process has never been tested with high sulfur fuels.³⁹ This process has been successfully demonstrated with phosphogypsum and natural gas.^{39,55,59,60,61,62,63} Thus, its technical viability under these conditions is unknown. Also, pilot plant operation for the development of process design criteria will be needed. Thus, further development of this project will be continued in Phase II, wherein optimization and verification of this process can be obtained on a pilot scale by the use of high sulfur coal.

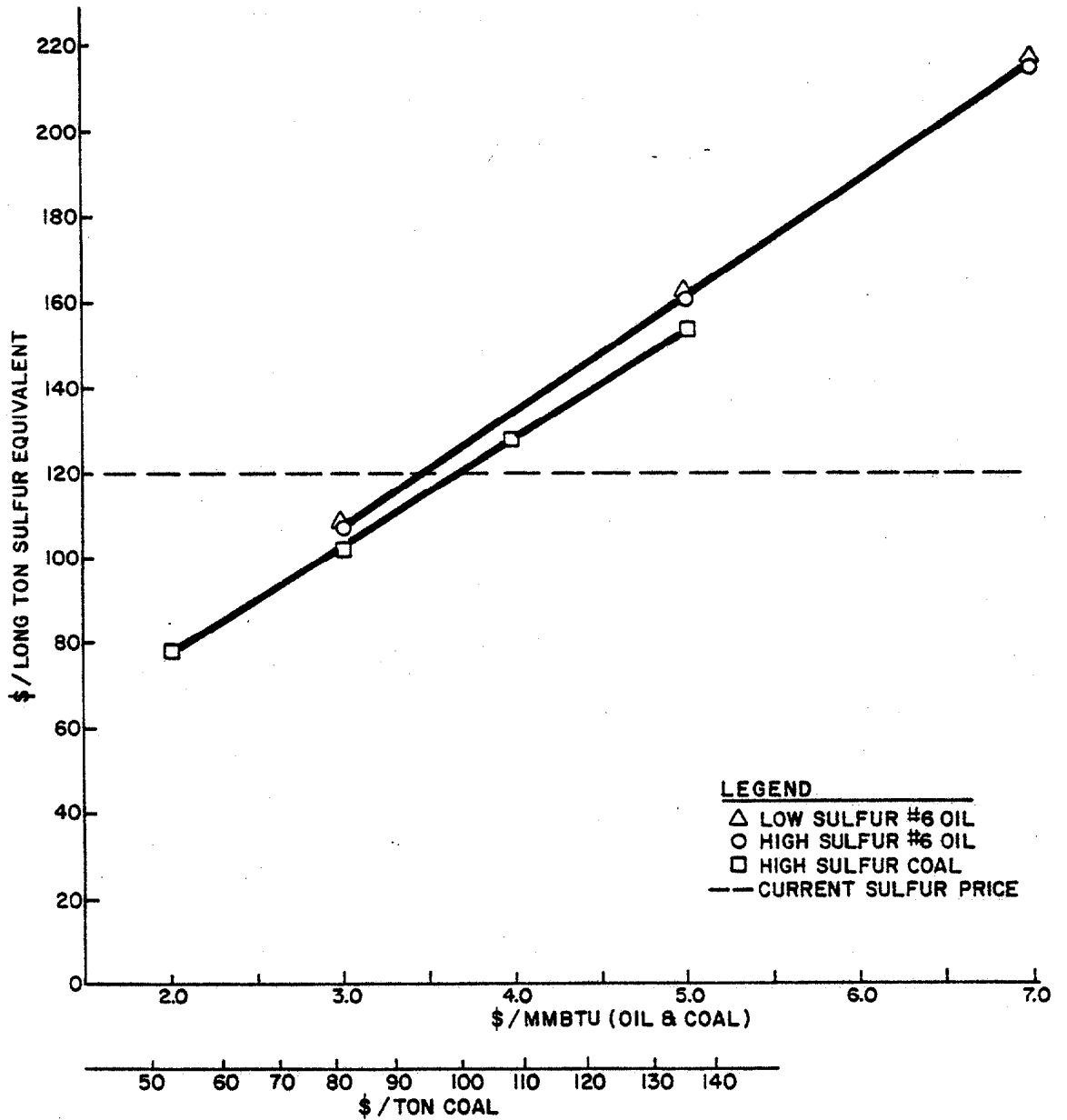
Process Description

Phosphogypsum from the phosphoric acid plant is fed to a rotary dryer for removal of surface moisture and water of crystallization (see Figure 8). The rotary dryer is vented to a baghouse where dust is removed prior to venting to the atmosphere.

The dried gypsum, now anhydrite, is conveyed by bucket elevator to storage silos. From the silos the anhydrite is fed to three disc pelletizers. The pelletized anhydrite is conveyed by bucket elevator to storage silos. The

Table VII
Fixed Capital Cost

Total Installed Equipment	\$19,500,000
Sales Tax	425,000
Labor Fringes	<u>875,000</u>
Total Direct Cost	\$20,800,000
Field Distribution	2,080,000
Engineering	<u>2,320,000</u>
Total Direct and Indirect Cost	\$25,200,000
Contingency	<u>2,500,000</u>
Total Fixed Capital Cost	<u><u>\$27,700,000</u></u>



**FIGURE 4 . Iowa State University Process
Total operating cost without lime by-product credit
vs. fuel costs.**

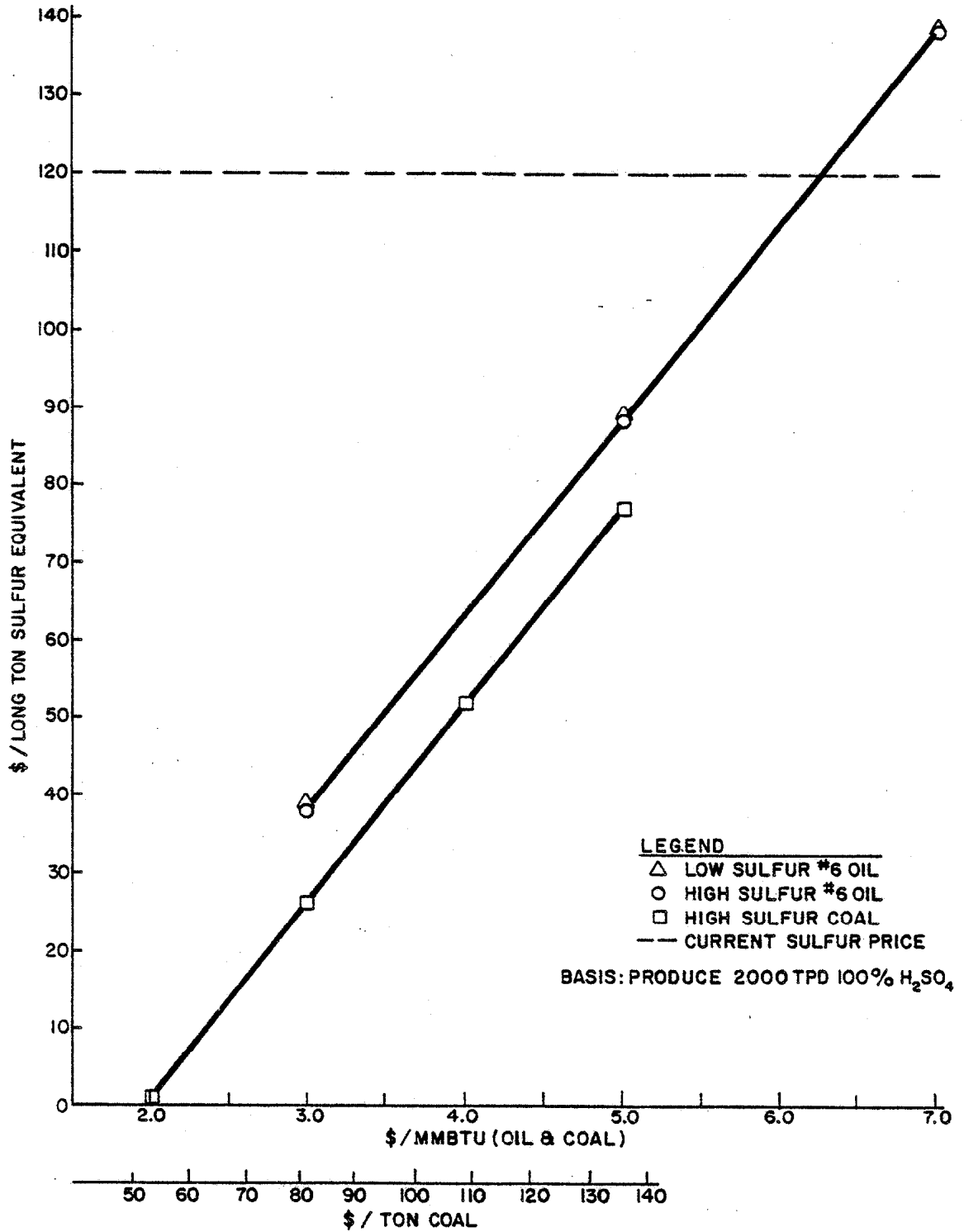


FIGURE 5. Iowa State University Process
Total operating cost with \$40/ton lime by-product credit
vs. fuel costs.

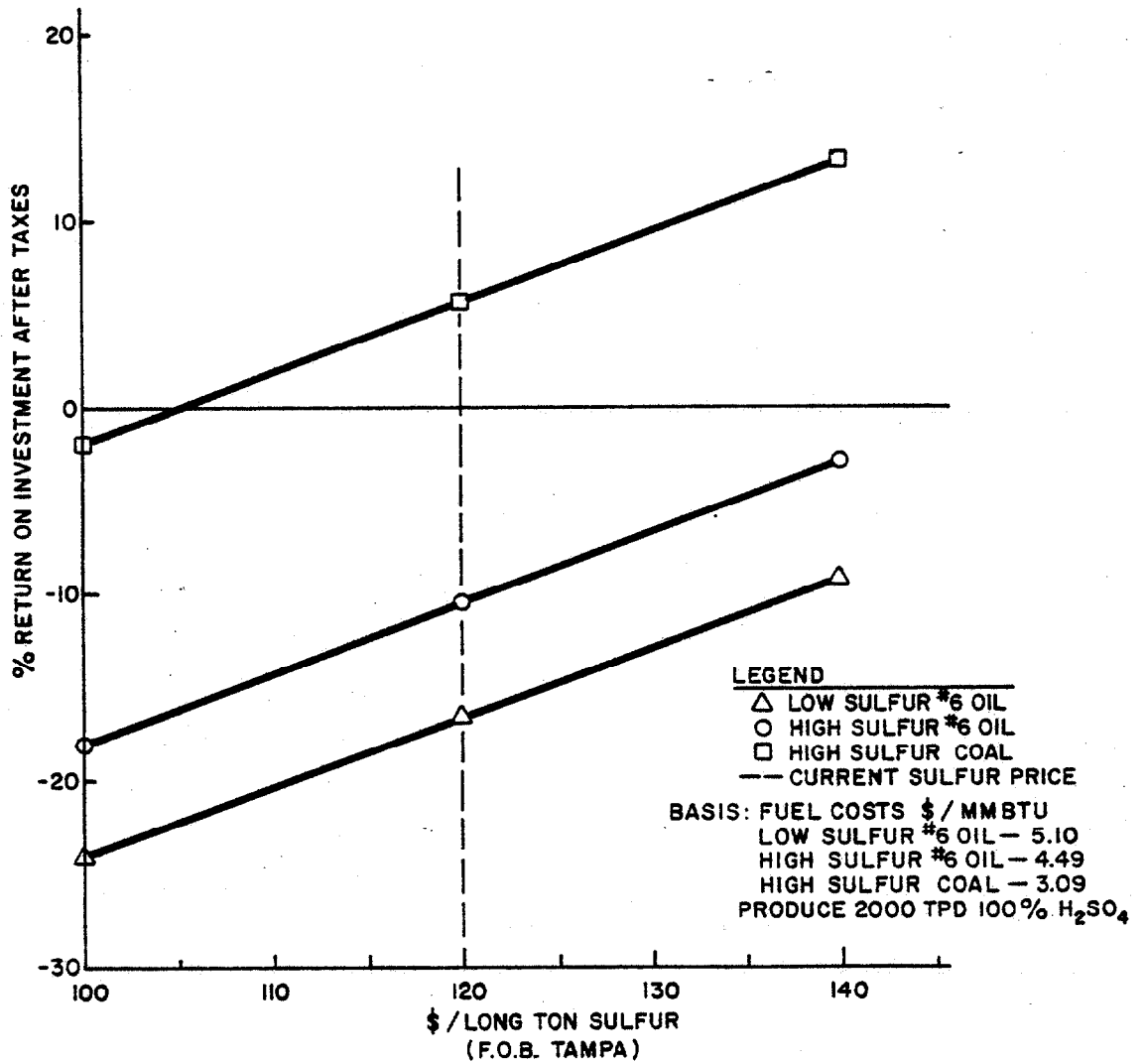


FIGURE 6. Iowa State University Process
% Return on investment after taxes without
lime by-product credit vs. sulfur cost.

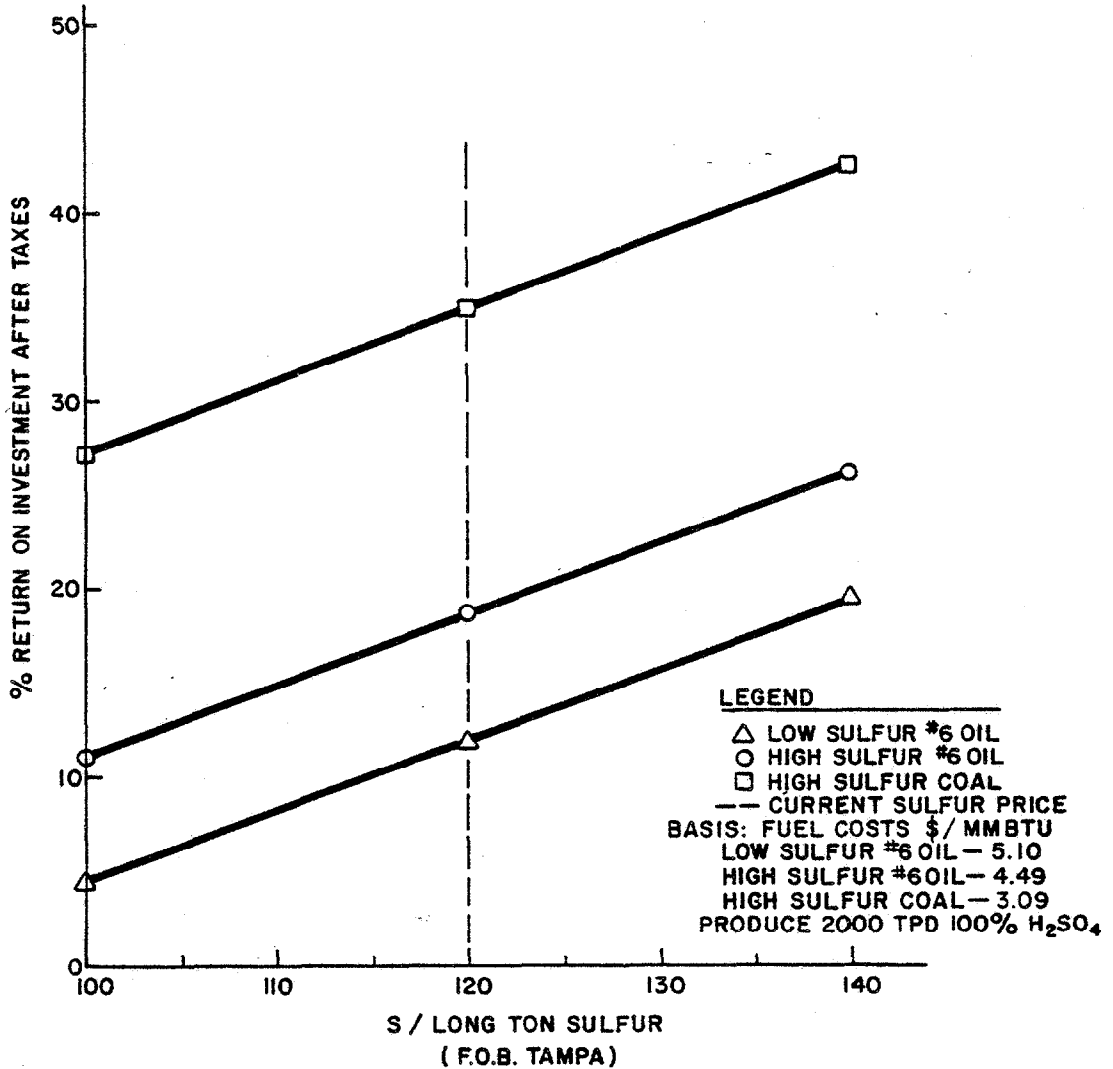


FIGURE 7. Iowa State University Process
% Return on investment after taxes with
\$40/ton lime by-product credit vs. sulfur cost.

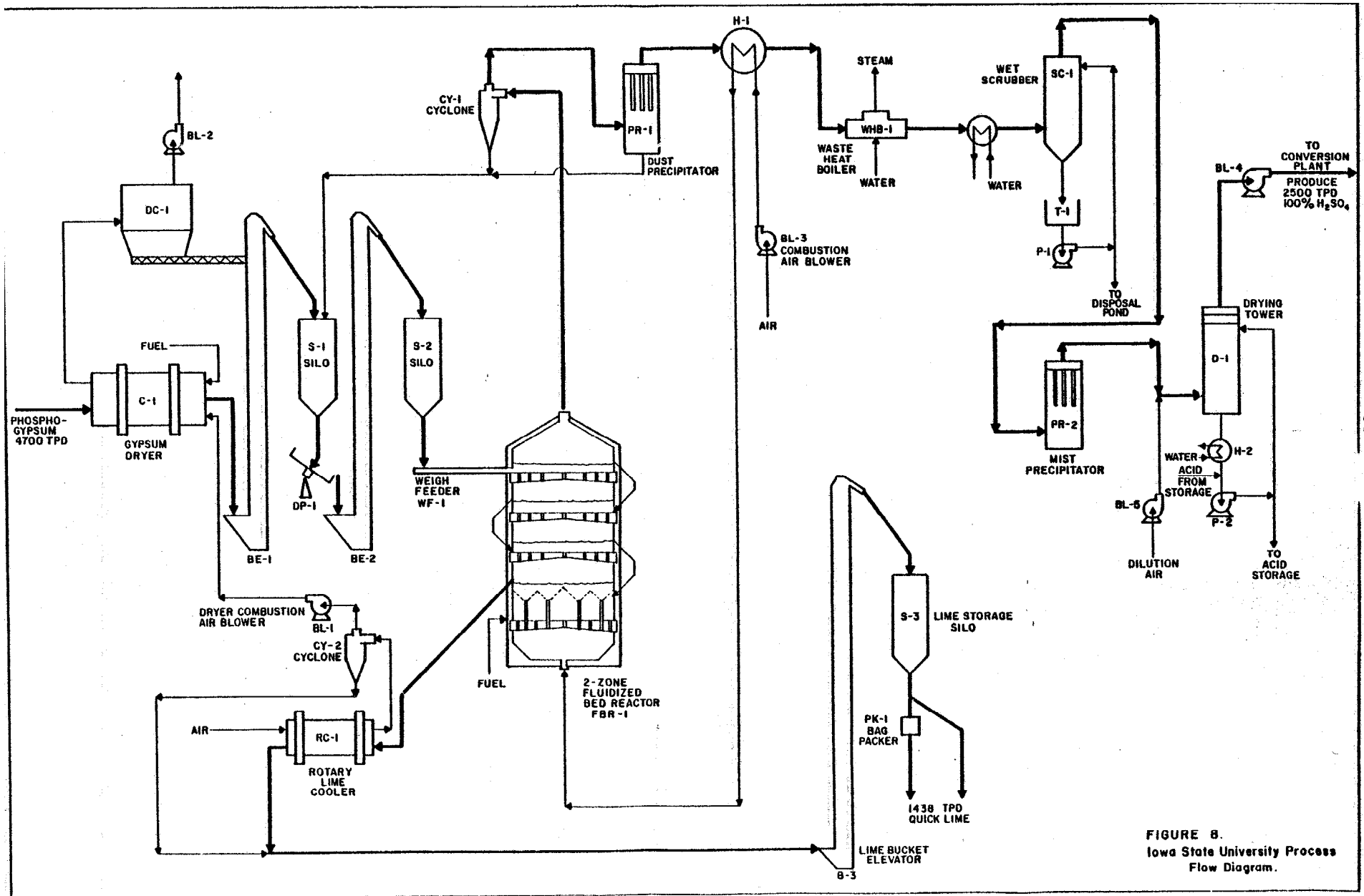


FIGURE 8.
Iowa State University Process
Flow Diagram.

pelletized anhydrite is fed to three (3) two-zone, fluidized bed reactors, each with three pre-heating stages.

The reduction-oxidation reactions take place in the two-stage fluidized bed reactors.^{39,55,59,61,62} The quicklime by-product is removed by overflow pipe to a rotary cooler. Cooling air is then used as combustion air in the gypsum dryer. From the cooler, the lime is conveyed by bucket elevator to the lime storage silo for storage prior to either bagging or bulk shipment,

The offgas from the reactor, after passing through the three preheater stages, passes through two cyclones which remove the majority of entrained dust. The remaining fine dust is removed in an electrostatic precipitator. This dust is returned to the anhydrite storage silo which feeds the pelletizers. The hot gas then passes through a heat exchanger where the combustion air for the reactor is preheated.

Further heat recovery is obtained by passing the hot gas through a waste heat boiler where steam (150 psig) is generated. The gas is cooled by water prior to entering a wet scrubber where the remaining dust is removed. The sludge from the scrubber is pumped to a disposal pond.

The scrubbed gas is then passed through a mist precipitator to remove droplets of impure sulfuric acid. Air is added after the mist precipitator to increase the oxygen content of the gas to the level required by the conversion plant. The gas is then dried in a tower using 93 percent sulfuric acid to remove the remaining moisture prior to the conversion plant. Part of the diluted acid is returned to storage, with the make-up coming from the acid production unit.

The main alteration to the original ISU process is the use of phosphogypsum as feedstock and high sulfur coal as the fuel source rather than natural gas and natural gypsum or anhydrite.^{35,36,37,38,39,55,59,60,61,62} The impure state of the phosphogypsum as it is currently produced in the phosphoric acid process requires some pretreatment in the form of sizing, washing and dewatering.^{39,55} One of the main differences is the requirement for pelletization or briquetting of the phosphogypsum feed to the reactor, in contrast to natural gypsum or anhydrite which requires sizer reduction only.^{39,55} It is possible that further modifications of the reaction conditions will be required as a result of using phosphogypsum and high sulfur coal in place of natural gypsum and natural gas.³⁹

The demonstration showed that by using phosphogypsum in place of natural gypsum, very little modification to the reaction conditions were necessary.

Economic Analysis with Alternate Fuels

Preliminary Capital Cost Estimate - This capital cost estimate includes only the fixed capital costs of the battery limits plant shown on the flow diagram, and the fuel supply system. The sulfuric acid plant capital cost is not included nor is any capital cost for washing or sizing the phosphogypsum, which may be necessary.

The fixed capital cost was developed on the basis that the plant is an addition to an existing facility. Working capital and offsites were not included. The equipment and motor lists used for capital cost estimates are contained in the appendix.

Operating Cost Estimate - The operating costs were estimated using three different fuels: low-sulfur #6 fuel oil, high-sulfur #6 fuel oil, and high sulfur coal. The operating costs summarized with and without credit for the by-product lime on Tables VIII through XIII.

These operating costs include costs in the gypsum disposal and conversion areas only; they do not include costs in the sulfuric acid plant. However, they do include the loss of the steam credit from substituting gypsum for liquid sulfur.

The impact of fuel cost is illustrated on Figures 4 and 5. Without any credit for the by-product lime and the current sulfur and fuel prices, high-sulfur coal is the only viable fuel for this process. However, when a credit of \$40 per ton of by-product lime is taken, all three fuels are viable, although the high-sulfur coal again gives the lowest operating cost.

Return on Investment - Return on investment after taxes was calculated as shown below:

$$\begin{aligned} \text{Gross Savings} &= \text{Liquid Sulfur Cost} - \text{Total Operating Cost} \\ &= (\$/\text{long ton S (FOB Tampa)}) - (\$/\text{long ton S equivalent}) \\ \text{Taxes} &= \text{Gross Savings} \times 48\% \\ \text{Net Savings} &= \text{Gross Savings} - \text{Taxes} \\ \text{Percent Return on Investment} &= \frac{\text{Net Savings}}{\text{Total Fixed Capital Cost}} \times 100\% \end{aligned}$$

The effect of sulfur price is evident in Figures 6 and 7. Without taking a credit for by-product lime (see Figure 6), the only viable fuel is high sulfur coal, as both- high- and low-sulfur #6 fuel oil are not profitable at current fuel and sulfur prices. With present fuel cost, low sulfur #6 oil does not break even until sulfur reaches \$165/long ton-; high sulfur #6 oil does not break even until sulfur reaches \$147/long. ton.

Taking a credit of \$40/ton of lime (see Figure 7) makes all three fuels profitable; however, at a sulfur price of \$120/long ton, high-sulfur coal has a return on investment after taxes of 34.9 percent, whereas high-sulfur #6 oil has 18.6 percent and low-sulfur #6 oil has 12.1 percent.

These calculations clearly demonstrate that high-sulfur coal is the most profitable fuel to use with this process, as it is the only fuel that is profitable without any credit for the by-product lime and is twice as profitable as the next best fuel with a credit for the by-product lime.

Table VIII
ISU Process Operating Cost
Low Sulfur #6 Fuel Oil

	Amount/Ton of 100% H ₂ SO ₄	Cost/Unit of Input	\$/Ton of 100% H ₂ SO ₄
1.) Raw Materials			
Phosphogypsum (dry basis)	1.81	-0-	-0-
2.) Utilities			
a.) Electric Power	36.05 KWH	\$ 0.045	\$ 1.62
b.) Cooling Water	3.65 MGAL	0.04	0.15
c.) Fuel - Low Sulfur #6 Oil	7.59 MMBTU	5.10	38.71
d.) Steam Credit (150 psig)	1.82 MLB	4.37	-7.95
3.) Labor			
a.) Operating (2 men/shift + dayman)	0.03 MHR	7.00	0.21
b.) Supervisory & Analytical (40% of operating labor)			0.08
4.) Maintenance (5% of fixed capital/year)			2.06
5.) Indirect Costs			
a.) Depreciation (15 year straight-line)			2.75
b.) Taxes and Insurance (2% fixed capital/year)			0.82
c.) Plant Overhead (60% of labor cost)			0.17
6.) Loss of Liquid Sulfur Steam Credit	2 MMBTU	5.10	<u>10.20</u>
Total Cost			<u>\$48.82</u>
By-product Lime Credit	0.57 Ton	40.00	<u>-22.80</u>
Net Cost			<u><u>\$26.02</u></u>

Table IX
ISU Process Operating Cost
High Sulfur #6 Fuel Oil

	Amount/Ton of 100% H ₂ SO ₄	Cost/Unit of Input	\$/Ton of 100% H ₂ SO ₄
1.) Raw Materials			
Phosphogypsum (dry basis)	1.81	-0-	-0-
2.) Utilities			
a.) Electric Power	35.54 KWH	\$ 0.045	\$ 1.60
b.) Cooling Water	3.60 MGAL	0.04	0.14
c.) Fuel - High Sulfur #6 Oil	7.53 MMBTU	4.49	33.81
d.) Steam Credit (150 psig)	1.79 MLB	3.84	-6.87
3.) Labor			
a.) Operating (2 men/shift + dayman)	0.03 MHR	7.00	0.21
b.) Supervisory & Analytical (40% of operating labor)			0.08
4.) Maintenance (5% of fixed capital/year)			2.06
5.) Indirect Costs			
a.) Depreciation (15 year straight-line)			2.75
b.) Taxes and Insurance (2% fixed capital/year)			0.82
c.) Plant Overhead (60% of labor cost)			0.17
6.) Loss of Liquid Sulfur Steam Credit	2 MMBTU	4.49	8.98
Total Cost			<u>\$43.75</u>
By-product Lime Credit	0.57 Ton	40.00	<u>-22.80</u>
Net Cost			<u>\$20.95</u>

Table X
ISU Process Operating Cost
High Sulfur Coal

	Amount/Ton of 100% H ₂ SO ₄	Cost/Unit of Input	\$/Ton of 100% H ₂ SO ₄
1.) Raw Materials			
Phosphogypsum (dry basis)	1.81 Ton	-0-	-0-
2.) Utilities			
a.) Electric Power	35.35 KWH	\$ 0.045	\$ 1.59
b.) Cooling Water	3.58 MGAL	0.04	0.14
c.) Fuel - High Sulfur Coal	7.10 MMBTU	3.09	21.94
d.) Steam Credit (150 psig)	1.78 MLB	2.65	-4.72
3.) Labor			
a.) Operating (2 men/shift + dayman)	0.03 MHR	7.00	0.21
b.) Supervisory & Analytical (40% of operating labor)			0.08
4.) Maintenance (5% of fixed capital/year)			2.06
5.) Indirect Costs			
a.) Depreciation (15 year straight-line)			2.75
b.) Taxes and Insurance (2% fixed capital/year)			0.82
c.) Plant Overhead (60% of labor cost)			0.17
6.) Loss of Liquid Sulfur Steam Credit	2 MMBTU	3.09	<u>6.18</u>
Total Cost			<u>\$31.22</u>
By-product Lime Credit	0.57 Ton	40.00	<u>-22.80</u>
Net Cost			<u>\$ 8.42</u>

Table XI
ISU Process Operating Cost Comparison Low Sulfur #6

Total Operating Cost * for Low Sulfur #6 Oil (\$5.10/MMBTU)

A. Without credit for by-product lime

\$ 48.82 per ton H₂SO₄ produced
\$164.46 per long ton sulfur equivalent
\$ 26.53 per ton gypsum processed
\$ 97.77 per ton P₂O₅ produced

Percent return on investment after taxes = -16.8%

B. With credit of \$40.00 per ton for by-product lime

\$ 26.02 per ton H₂SO₄ produced
\$ 87.65 per long ton sulfur equivalent
\$ 14.14 per ton gypsum processed
\$ 52.11 per ton P₂O₅ produced

Percent return on investment after taxes = 12.1%

* All operating costs in gypsum disposal and conversion areas only. Does include loss of steam credit from substituting gypsum for liquid sulfur. Includes 15 year straight-line depreciation.

Note: Does not include cost of sulfuric acid plant.

Table XII
ISU Process Operating Cost Comparison High Sulfur #6

Total Operating Cost * for High Sulfur #6 Oil (\$4.49/MMBTU)

A. Without credit for by-product lime

\$ 43.75 per ton H₂SO₄ produced
\$147.38 per long ton sulfur equivalent
\$ 24.11 per ton gypsum processed
\$ 88.85 per ton P₂O₅ produced

Percent return on investment after taxes = -10.1%

B. With credit of \$40.00 per ton for by-product lime

\$ 20.95 per ton H₂SO₄ produced
\$ 70.58 per long ton sulfur equivalent
\$ 11.54 per ton gypsum processed
\$ 42.55 per ton P₂O₅ produced

Percent return on investment after taxes = 18.6%

* All operating costs in gypsum disposal and conversion areas only. Does include loss of steam credit from substituting gypsum for liquid sulfur. Includes 15 year straight-line depreciation.

Note: Does not include cost of sulfuric acid plant.

Table XIII
ISU Process Operating Cost Comparison High Sulfur Coal

Total Operating Cost * for High Sulfur Coal (\$3.09/MMBTU)

A. Without credit for by-product lime

\$ 31.22 per ton H₂SO₄ produced
\$105.17 per long ton sulfur equivalent
\$ 17.29 per ton gypsum processed
\$ 63.74 per ton P₂O₅ produced

Percent return on investment after taxes = 5.7%

B. With credit of \$40.00 per ton for by-product lime

\$ 8.42 per ton H₂SO₄ produced
\$ 28.36 per long ton sulfur equivalent
\$ 4.66 per ton gypsum processed
\$ 17.19 per ton P₂O₅ produced

Percent return on investment after taxes = 34.9%

* All operating costs in gypsum disposal and conversion areas only. Does include loss of steam credit from substituting gypsum for liquid sulfur. Includes 15 year straight-line depreciation.

Note: Does not include cost of sulfuric acid plant.

Engineering Summary

Presently, numerous processes exist either theoretically or experimentally capable of producing valuable by-products such as plaster, wallboard, cement, sulfur, etc. from phosphogypsum. However, unlike several European countries and Japan, industry in the United States has avoided large scale exploitation of this gypsum due to the availability of cheap, high-grade raw materials and energy. With the current increases in the cost of energy and the rapid depletion of mineral resources, industry in this country is now in a favorable position to exploit new technology in this area, provided the technology is economically and environmentally acceptable.

One of the most promising technologies is the ISU process, which produces quicklime and sulfur dioxide by thermal decomposition of calcium sulfate in a two-zone fluidized bed reactor. The main innovation of this process, not previously tried in gypsum decomposition, is the use of two zones operating with the same fluidized bed. That is, the use of a reducing zone at the bottom of the bed with the upper portion of the bed serving as an oxidizing zone. The use of two-zones within the same fluidized bed is the only non-standard unit operation involved in this process. This exploitation of standard technology, with a minimum use of innovation in the way of equipment design, greatly decreases the difficulties and time required for complete, full-scale development.

Preliminary economics indicate this process is feasible, without any credit for the by-product lime, under the current economic conditions. This factor is a very important advantage for the ISU process in that it is not subject to multiple market fluctuations, the economics depending mainly on the sulfur market. Such processes as the OSW-Krupp or Marchon process that require the sale of by-product portland cement are very susceptible to fluctuations in the building industry as well as in the sulfur market. Due to the large production of cement from such processes, its adoption is somewhat limited by building material market constraints, whereas the ISU process has no such dependence.

This process has been extensively⁶¹ investigated for the last 25 years at ISU, using natural gypsum and anhydrite with natural gas as the fuel. The process has been successfully demonstrated using natural gypsum and phosphogypsum with natural gas as the fuel.

The novelty of the proposed process approach comprises the use of low-priced, abundant, high-sulfur coal as the fuel for the decomposition of phosphogypsum. Through this process, the combined environmental problems associated with phosphogypsum disposal and high-sulfur coal utilization can be resolved effectively by the recovery of urgently needed sulfur for the fertilizer industry. This reclamation of the sulfur chemically bound in the gypsum effectively "closes the loop" of the sulfur usage in a fertilizer plant, thereby conserving a valuable natural resource. The only additional sulfur input that will be necessary is the small make-up required to cover losses in the facility.

This process eliminates the need for disposal of gypsum, as it is produced only as an intermediate and not as a final product. Therefore, the areas now used for gypsum disposal will be available for other uses and the associated problems of containing and controlling the disposal areas will be eliminated as well.

The use of high-sulfur coal as the energy source for this process eliminates any dependence on fuels that are currently in high demand, such as low-sulfur fuel oil or coal and natural gas. This allows for more efficient utilization of limited energy and mineral resources in an environmentally acceptable fashion. At present, there is little or no demand for high sulfur coal, which is plentiful, thereby insuring a secure, low-cost fuel supply for this process.

The lime produced has many possible applications. It can be used for waste water neutralization, both on and off site, or used for slimes neutralization-consolidation on site. This lime could possibly be used as a raw material for cement manufacture at an adjacent facility, thereby reducing Florida's dependence on outside sources of cement and lime.

The use of each ton of high-sulfur coal reduces the importation of fuel oil by approximately 3.9 barrels. Therefore, a facility producing 1,000 tpd of P_2O_5 would save 3,100 barrels of oil per day by using high-sulfur coal that is currently in very low demand due to the environmental problems concerning its combustion. The use of lime for a multitude of processes and products would become possible with this new source of readily available lime, thereby promoting new industrial development.

As a part of ZW's current research project with FIPR, a bench-scale demonstration of this process, using phosphogypsum and natural gas, was held on August 25, 1981 at ISU. This demonstrated the basic technical feasibility of the application of this process to phosphogypsum. However, due to the limited scope of this demonstration, many technical aspects concerning the future exploitation of this process were not investigated, such as the effects of the various impurities and their concentrations in the many different phosphogypsums produced in this area of Florida. Therefore, a pilot-plant, process development investigation is required (Phase II).

Many engineering design criteria must also be investigated and quantified. These consist of items such as the effects of variations in impurities and temperature on the reaction rate, the type of feed preparation used as well as the effects any impurities therein contained in the high-sulfur coal may have on the products. Once these parameters are defined, the engineering and economics must be revised to include any new information that was developed to ensure optimum utilization.

From this preliminary study it was concluded that for a large scale solution of the phosphogypsum disposal problem the ISU process holds the greatest promise of success. However, for a small number of producers the CdF Chemie and OSW-Krupp processes have the potential for converting the phosphogypsum into saleable products.

Currently most natural gypsum users in the State of Florida import the gypsum from Nova Scotia, incurring a significant transportation cost. The preliminary economics developed for the CdF Chemie process indicate the feasibility of producing a stable hemihydrate product comparable to that from natural gypsum for the production of wallboard and plaster. Due to the limited markets for such products, only a small portion of the total phosphogypsum could be disposed of in this manner, for example, the world's largest wallboard plant located in Jacksonville, Florida consumes on the order of 800,000 tons per year of gypsum. This amount of gypsum could be produced by a 1,000 tpd P_2O_5 phosphoric acid plant in a little over half a year.

The OSW-Krupp process to produce portland cement and SO_2 from phosphogypsum offers the potential for several producers in different areas of the state to recover the contained sulfur and eliminate the gypsum disposal problem. This process had the least favorable economics of those studied in detail. The main drawbacks to the implementation of this process are the dependence on two markets to provide profitability, sensitivity to gypsum impurities as related to cement purity and low return on investment, even with full credit for the by-product cement.

There is some uncertainty as to whether or not a high-grade portland cement can be produced from this process. The current operators of this process have difficulty consistently meeting specifications which are less strict than those in the U.S. These additional quality specification limitations required of a cement product versus that of a lime product to be used captively by the producer are a disadvantage compared to using the ISU process. Fewer feed preparation steps are involved in the ISU process, where impurity removal is not as critical. This is an advantage of the ISU process over many other processes.

A plant sized to handle the complete output of gypsum would produce a large amount of portland cement compared to the capacity of a standard portland cement plant. This introduces difficulties, in that a fertilizer producer would not immediately be in a position to market large amounts of cement, leading to further difficulties for the operator. The best case for implementation of this process would involve a joint venture by a cement producer and a fertilizer manufacturer.

Although the preliminary investigation indicated that the agricultural applications were not of a sufficient magnitude to warrant detailed analysis, natural gypsum is a valuable material for soil amendments. Phosphogypsum is of the same value and, in addition, contains some phosphorus nutrient. Several other elements, in particular, iron as Fe_2O_3 , are commonly present in trace quantities. Apparently no contaminants, including fluorine and radium -226, are present in sufficient amounts to cause problems.

Where phosphogypsum can compete in price with mined natural gypsum (land plaster), it should be marketed. In Florida, for instance, the major cost in phosphogypsum is shipping.

Phosphogypsum may also be of value for direct reclamation of clay settling areas. One of the major problems in the use of such areas is poor tillage properties, which phosphogypsum may improve. However, limited data exists to support such a contention, and field research should be completed before marketing efforts commence.

The uses of phosphogypsum in agriculture are too limited to alleviate a significant portion of the waste disposal problem on an international or even statewide basis. However, the potential benefits from phosphogypsum application in several cases (Ca source, sulfur source, and land reclamation) are significant enough that agricultural markets should be developed. Although this would not remedy the waste disposal problems associated with the material, the possible increase in agricultural productivity can benefit both farmers and purchasers of agricultural products. For this reason, phosphogypsum should be made available to agricultural interests at a price as nearly competitive with other materials as possible.

DEMONSTRATION

The results of the literature search and preliminary economics indicated that the most promising process, under current conditions, is the ISU process for thermal decomposition of phosphogypsum to produce SO_2 and quicklime. After discussions with Dr. T. D. Wheelock of the ISU Chemical Engineering Department, the inventor of the process, it was decided to pursue a demonstration using phosphogypsum with natural gas as the fuel. In order to maximize the limited resources of the project, the existing equipment at ISU was chosen for the demonstration. The existing fluidized bed reactor, along with the controls, were rebuilt and improved. After a period of mechanical shakedown using natural anhydrite, tests were successfully run with phosphogypsum.

The phosphogypsum was washed, dried, screened at 65-mesh to remove the major contaminants, and then briquetted, crushed and sized to -12, +60 mesh. The material was then fed to the fluid bed reactor using a pneumatic weigh feeder.

The demonstration/seminar was given on Tuesday, August 25, 1981 at ISU with about 20 representatives of Industry present. A seminar was held to discuss the chemical, engineering and economic aspects of the process along with a tour of the facilities. The program is presented below:

- | | |
|---------------|--|
| 9:00 - 9:15 | Brief introduction and welcome by Dr. D. P. Borris, Executive Director of the Florida Institute of Phosphate Research. |
| 9:15 - 9:45 | Description of demonstration and facilities by Dr. T. D. Wheelock. |
| 9:45 - 10:15 | Inspection of fluid bed unit and bench scale facilities. |
| 10:15 - 11:30 | Continuation of presentation by Dr. Wheelock (Physical and Chemical parameters) |
| 11:30 - 1:30 | Lunch |
| 1:30 - 2:00 | Inspection of fluid bed unit. |
| 2:00 - 3:00 | Engineering and Economic parameters of the process presented by Mr. A. P. Kouloheris, ZW. |
| 3:00 - 3:45 | Phase II development program presented by Mr. A. P. Kouloheris, ZW. |
| 3:45 - 4:30 | Question and Answer period. |

CONCLUSIONS AND RECOMMENDATIONS

The ISU process for the production of SO_2 and lime from phosphogypsum is the most promising solution to the gypsum disposal problem at this time. It has the potential for eliminating the production of waste gypsum as a final product and allows for recovery of sulfur, a valuable natural resource. It is recommended that the project be continued in Phase II to develop the technical and economic feasibility. This is necessary as the process has only been tested with phosphogypsum using natural gas as the fuel, rather than high-sulfur coal as has been envisioned in this project. It is also recommended that potential uses for the lime product be investigated.

The CdF Chemie process for the purification of phosphogypsum and conversion to hemihydrate for wallboard and plaster production could provide an outlet for a small amount of the total phosphogypsum production. It is recommended that further investigation of the market potential for this hemihydrate product be completed.

APPENDIX

OSW-Krupp
Design Criteria

- 1.) Production capacity - 2,500 TPD 100% H₂SO₄ @ 99% conversion in acid plant
- 2.) Phosphogypsum - 4,700 TPD (dry basis) 1,578,000 Ton/Year, (1,000 TPD P₂O₅ plant) (see Figure 1)
20% free moisture
1.6% impurities
78.4% CaSO₄ • 2H₂O
- 3.) Anhydrite (dried gypsum) bulk density - 50 lb./cu. ft.
- 4.) Pelletizer product - 90% +65 mesh
- 5.) Anhydrite Feed to Kiln - 60°F
- 6.) Fuel to Kiln - 60°F
- 7.) Combustion Air - 60°F
- 8.) Conversion of Phosphogypsum to Cement and SO₂ - 98%, Conservative Estimates
- 9.) Cooling Water - 86°F
- 10.) Dilution Air - 95°F
- 11.) 93% Sulfuric Acid at Drying Tower - 95°F
- 12.) Low Sulfur #6 Fuel Oil Analysis - 87.26% C, 10.49% H₂, 0.64% O₂, 0.84% S,
Heating Value = 17,619 BTU/lb

OSW-Krupp Process Equipment List

<u>Equipment Number</u>	<u>Quantity</u>	<u>Description</u>
D-1	1	Gypsum Dryer
DC-1	1	Dryer Dust Collector
BL-1	1	Dust Collector Fan
BL-2	1	Dryer Combustion Air Blower
BE-1	1	Anhydrite Bucket Elevator
S-1	1	Additive Dryer Feed Silo
D-2	1	Additive Dryer
DC-2	1	Additive Dryer Dust Collector
BL-3	1	Additive Dust Collector Fan
BL-4	1	Additive Dryer Combustion Air Blower
BE-2	1	Additive Bucket Elevator
BC-1	1	Additive Belt Conveyor
S-2	1	Coke Storage Silo
S-3	1	Clay Storage Silo
S-4	1	Sand Storage Silo
S-5, A, B	2	Anhydrite Storage Silo
WF-1	1	Coke Weigh Feeder
WF-2	1	Clay Weigh Feeder
WF-3	1	Sand Weigh Feeder
WF-4, A-B	2	Anhydrite Weigh Feeder
BC-2	1	Raw Mix Conveyor
M-1	1	Raw Mix Mill
DC-3	1	Raw Mix Mill Dust Collector
BL-5	1	Raw Mix Dust Collector Fan
S-6	1	Raw Mix Storage Silo
DP-1, A-C	3	Raw Grind Pelletizer
BE-3	1	Raw Grind Bucket Elevator
K-1, A-B	2	Krupp Kiln
PR-1	1	Dry Precipitator
H-1	1	Offgas Cooler
SC-1	1	Wet Scrubber
T-1	1	Scrubber Tank
P-1	1	Scrubber Circulation Pump
PR-2	1	Mist Precipitator
BL-10	1	Air Blower
DT-1	1	Drying Tower
BL-11	1	Conversion Plant Blower
H-2	1	Acid Cooler
P-2	1	Drying Tower Pump
CL-1	2	Clinker Cooler
BL-6	2	Clinker Cooler Air Blower
S-7	1	Additive Anhydrite Storage Silo
WF-5	1	Additive Anhydrite Weigh Feeder
BC-3	1	Additive Anhydrite Belt Conveyor
M-2	1	Finish Mill
DC-4	1	Finish Mill Dust Collector
BL-7	1	Finish Mill Collector Fan
BL-8	1	Cement Pneumatic Conveyor Blower

<u>Equipment Number</u>	<u>Quantity</u>	<u>Description</u>
S-8, A, B	2	Finished Product Storage Silos
DC-5	1	Finished Product Duct Collector
BL-9	1	Finished Product Dust Fan
PK-1	1	Cement Bag Packer
FS-1	1	Fuel Supply System

OSW Krupp Process Motor List

<u>Equipment Number</u>	<u>HP</u>
D-1 (includes BL-2)	500
DC-1 (includes BL-1)	200
BE-1	30
D-2	65
DC-2 (includes BL-3)	25
BL-4	35
BE-2	5
BC-1	1
WF-1	1
WF-2	1
WF-3	1
WF-4, A, B	6
BC-2	5
M-1	3,500
DC-3 (includes BL-5)	25
DP-1, A-C	300
BE-3	45
K-1, A, B (includes BL-6)	1,600
P-1	10
BL-10	700
BL-11	2,000
P-2	40
WF-5	6
BC-3	2
M-2	5,000
DC-4 (includes BL-7)	25
BL-8	120
DC-5 (includes BL-9)	25
PK-1	1
	<hr/>
TOTAL	14,274 HP

CdF Chemie
Design Criteria

- 1.) Phosphogypsum - 4,700 TPD (dry basis), 1,578,000 Ton/Year, (1,000 TPD P₂O₅ plant) (see Figure 1)
 - 20% free moisture
 - 1.6% impurities
 - 78.4% CaSO₄ • 2H₂O
- 2.) Hemihydrate bulk density - 60 lb./cu ft.
- 3.) Hemihydrate product
 - 85% -100 mesh
 - 95% +200 mesh
- 4.) Hemihydrate Feed to Dryer - 60°F
- 5.) Fuel to Dryer - 60°F
- 6.) Combustion Air - 60°F
- 7.) Conversion of Phosphogypsum to Hemihydrate - 98%, Conservative Estimates
- 8.) Cooling Water - 86°F
- 9.) Low Sulfur #6 Fuel Oil Analysis - 87.26% C, 10.49% H₂, 0.64% O₂, 0.84% S, Heating Value = 17,619 BTU/lb.

CdF Chemie Process Equipment List

<u>Equipment Number</u>	<u>Quantity</u>	<u>Description</u>
T-1	1	Wash Tank 1
AG-1	1	Tank 1 Agitator
P-1	1	Screen Feed Pump
VS-1, A-H	8	Vibrating Screens
PB-1	1	Overs Pump Box
P-8	1	Oversize Pump
T-2	1	Wash Tank 2
AG-2	1	Tank 2 Agitator
P-2	1	Primary Cyclone Feed Pump
HC-1	106	Primary Cyclones
T-3	1	Wash Tank 3
AG-3	1	Tank 3 Agitator
P-3	1	Secondary Cyclone Feed Pump
HC-2	106	Secondary Cyclones
P-9	1	Lime Slurry Pump
T-4	1	Neutralization Tank
AG-4	1	Neutralization Tank Agitator
P-4	1	Belt Filter Pump
BF-1, A-G	7	Vacuum Belt Filter
RC-1, A-G	7	Filtrate Receiver
VP-1, A-G	7	Vacuum Pump
T-5	1	Filtrate Tank
P-5	1	Filtrate Recycle Pump
BN-1	1	Wet Gypsum Feed Bin
D-1, A,B	2	Gypsum Flash Dryer 1
C-1, A,B	2	Dryer 1 Cyclone
B-1, A,B	2	Dryer 1 Combustion Air Blower
D-2, A,B	2	Gypsum Flash Dryer 2
B-2, A,B	2	Dryer 2 Combustion Air Blower
BN-2	1	Dry Gypsum Bin
C-2, A,B	2	Dryer 2 Cyclone
BN-3	1	Calcined Gypsum Bin
D-3	1	Gypsum Flash Dryer 3
C-3	1	Dryer 3 Cyclone
B-3, A,B	2	Cool Recycle Air Blower
B-4, A,B	2	Hot Recycle Air Blower
BN-4	1	Hemihydrate Bin
H-1, A,B	2	Dryer 1 Fuel Heat Exchanger
H-2, A,B	2	Dryer 1 Combustion Air H.E.
H-3, A,B	2	Dryer 2 Fuel H.E.
H-4, A,B	2	Dryer 2 Combustion Air H.E.
SC-1	1	Wet Scrubber
B-5	1	Wet Scrubber Blower
T-6	1	Scrubber Tank
P-7	1	Scrubber Circulation Pump
P-6	1	Scrubber Recycle Water Pump

CdF Chemie Process Motor List

<u>Equipment Number</u>	<u>HP</u>
AG-1	25
P-1	75
VS-1	16
P-8	100
AG-2	25
P-2	125
AG-3	25
P-3	125
P-9	2
AG-4	25
P-4	125
BF-1	560
VP-1	1,400
P-5	60
B-1	300
B-2	250
B-3	800
B-4	1,400
B-5	450
P-7	20
P-6	<u>20</u>
Total	5,928 HP

ISU Process
Design Criteria

- 1.) Production capacity - 2,500 TPD 100% H_2SO_4 @ 99% conversion in acid plant
- 2.) Phosphogypsum - 4,700 TPD (dry basis) 1,578,000 Ton/Year, (1,000 TPD P_2O_5 plant) (see Figure 1)
20% free moisture
1.6% impurities
78.4% $CaSO_4 \bullet 2H_2O$
- 3.) Anhydrite (dried gypsum) bulk density - 50 lb./cu. ft.
- 4.) Anhydrite to pelletizers
85% -100 mesh
95% +200 mesh
- 5.) Pelletizer product - 90% +65 mesh.
- 6.) Anhydrite Feed to Reactor - 60°F
- 7.) Fuel to Reactor - 60°F
- 8.) Combustion Air - 60°F
- 9.) Conversion of Phosphogypsum to Quicklime and SO_2 - 98%, Conservative Estimates
- 10.) Cooling Water - 86°F
- 11.) Dilution Air - 95°F
- 12.) 93% Sulfuric Acid at Drying Tower - 95°F
- 13.) Low Sulfur #6 Fuel Oil Analysis - 87.26% C, 10.49% H_2 , 0.64% O_2 , 0.84% S, Heating Value = 17,619 BTU/lb
- 14.) High Sulfur #6 Fuel Oil Analysis - 84.67% C, 11.02% H_2 , 0.38% O_2 , 3.97% S, Heating Value = 17,342 BTU/lb
- 15.) High Sulfur Coal Analysis - 73.7% C, 5.0% H_2 , 8.0% O_2 , 4.4% S, Heating Value = 11,800 BTU/lb

Iowa State University Process Equipment List

<u>Equipment Number</u>	<u>Quantity</u>	<u>Description</u>
C-1	1	Gypsum Dryer
DC-1	1	Dryer Dust Collector
BL-2	1	Dust Collector Fan
BE-1	1	Anhydrite Bucket Elevator
S-1, A, B	2	Anhydrite Storage Silos
DP-1, A - C	3	Disc Pelletizers
BE-2	1	Pelletized Anhydrite B.E.
S-2, A, B	2	Pelletized Anhydrite Storage Silos
WF-1, A - C	3	Anhydrite Weigh Feeders
FBR-1, A - C	3	Fluidized Bed Reactors
BL-3, A - C	3	Combustion Air Blowers
CY-1, A - F	6	Cyclones
H-1, A - C	3	Offgas Heat Exchangers
WHB-1	1	Waste Heat Boiler
H-3	1	Offgas Cooler
SC-1	1	Wet Scrubber
T-1	1	Scrubber Tank
P-1	1	Scrubber Circulation Pump
PR-1	1	Mist Precipitator
D-1	1	Drying Tower
H-2	1	Acid Cooler
P-2	1	Drying Tower Pump
BL-5	1	Air Blower
BL-4	1	Conversion Plant Blower
RC-1	1	Rotary Lime Cooler
CY-2, A, B	2	Cyclones
BL-1	1	Rotary Dryer Combustion Blower
BE-3	1	Lime Bucket Elevator
S-3	1	Lime Storage Silo
PK-1	1	Lime Bag Packer
FS-1	1	Fuel Supply System

Iowa State University Process Motor List

<u>Equipment Number</u>	<u>HP</u>
C-1 (includes BL-1)	100
DC-1 (includes BL-2)	200
BE-1	30
DP-1, A - C	300
BE-2	30
WF-1, A - C	6
BL-3, A - C	600
P-1	10
P-2	40
BL-5	700
BL-4	2,000
BE-3	15
PK-1	1
	<hr/>
Total	4,032 HP

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