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PHOSPHOGYPSUM

A Review of the Florida Institute of Phosphate Research Programs to Develop Uses for Phosphogypsum

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INTRODUCTION

Phosphogypsum disposal was a very simple matter in the early days of the industry. If at all possible, you located your plant near the ocean or on a river and dunped the phosphogypsum into the sea or the river. If you were foolish enough to locate where water disposal was not possible, you suffered the economic penalty of having to stack the phosphogypsum on dry land. The industry developed first in Europe and due to a number of circumstances, phosphogypsum disposal of any type did not create a problem because:

(1) Plants had very low capacities, often producing only 25 tons per day of P_2O_5 (typical plant today is rated at 1000 tons per day) with no more than 120 tons per day of gypsum for disposal.

(2) Since gypsum is slightly soluble in water, river dumping did not create problems for river traffic because there was no accumulation of material to block the channel.

(3) Ocean disposal was ideal since gypsum is more soluble in salt water than it is in fresh water. While ocean disposal has now been restricted, this disposal method has been demonstrated to have minimum adverse environmental effects when done properly.

(4) Land disposal was not a major problem due to the small quantities of material to be handled.

While some of the earlier plants in this country practiced water disposal, most of the phosphogypsum produced here has been piled on land. Again, it must be remembered that plant size (capacity) was a big factor in determining if there was a phosphogypsum problem With the advent of 300, 500, 1000 and even 4000-5000 tons per day $P_2 O_5$ plants, the phosphogypsum disposal problem took on new aspects. While most of the rest of the world looked at phosphogypsum as a valuable raw material and developed processes to utilize it in chemical manufacture and building products, this country blessed with abundant low-cost natural gypsum - piled the phosphogypsum up rather than bear the additional expense of utilizing it as a raw material. It should be noted that during most of this time period the primary reason phosphogypsum was not used for construction products in this country was because it contained small quantities of fluorine and P_2O_5 as impurities and fuel was required to dry it before it could be processed. It has only been in recent years that the question of radioactivity has been raised and this question now influences every decision relative to potential use in building products in this country.

Phosphogypsum utilization has evolved along three broad use groupings:

- (1) Chemical raw material
- (2) Agricultural applications
- (3) Construction materials

Each of these uses will be considered in more detail, but it should be pointed out that for years Florida has not been in the forefront of the efforts to utilize phosphogypsum The impetus to develop uses for this material has come from countries where land area for phosphogypsum storage is in very short supply and/or very expensive, or where the cost to utilize natural gypsum exceeded the cost of utilizing the phosphogypsum In most of this country, and specifically in Florida, economic incentives to develop uses for phosphogypsum have not existed. A common theme can be found in the worldwide history of the development, adoption and abandonment of phosphogypsum utilization schemes - economic incentive. This critical influence of economic incentives will be obvious in the following discussions.

<u>Chemical Raw Material</u> Thermal Processing

<u>Background.</u> Thermal processing of gypsum to produce sulphur was first practiced commercially in Germany during the first World War when their sulphur supply was disrupted by the Allied blockade. While numerous process modifications have been proposed and/or practiced since that time, the basic requirements for successfully applying this technology remains unchanged. All processes require at a minimum

(1) Gypsum Natural or by-product gypsum can be used.

(2) Fuel. Any fuel can be used to heat the gypsum to reaction temperature, and over the years almost every common fuel has been used.

(3) A carbon source. Carbon is needed to react with the gypsum Carbon can come from any source, but most commonly, fuel in excess of that needed to heat the material to reaction temperature is used as the carbon source. Since carbon monoxide is considered to be one of the more reactive sources of carbon for the necessary reactions, incomplete combustion of the fuel is generally practiced to insure an adequate supply of this desirable reactant.

The basic reactions employed to produce sulphur are:

CaSO ₄ + 2C	\rightarrow CaS + 2CO ₂	(1)
$CaS + H_2O + CO_2$	\rightarrow CaCO ₃ + H ₂ S	(2)
2H ₂ S + 30 ₂	$\rightarrow 2SO_2 + 2H_2O$	(3)
$2H_2S + SO_2$	\rightarrow 3S + 2H ₂ 0	(4)

The thermal treatment of the gypsum is described by reaction (1). The calcium sulphide (CaS) solid exiting the thermal reactor is dropped into boiling water where it reacts with carbon dioxide to generate hydrogen

sulphide as shown in reaction (2), A portion of the H_2S is burned to produce sulphur dioxide (SO₂) in a third reaction vessel (reaction 3). Lastly, the balance of the H_2S reacts with the SO₂ to give sulphur. (Reactions 3 & 4 are the basis for the widely used Claus process that recovers by-product sulphur from "sour gases" in petroleum processing).

This process has been studied at various times since it was first used, and a modified process has recently been piloted in India. The only commercial application of this process was by Elcor Chemical during the late 1960's. After pilot plant development, a full-size plant utilizing natural gypsum calcined in a shaft kiln was placed in operation. While the plant did eventually operate successfully after overcoming many mechanical problems, falling prices for sulphur coupled with the high cost of the plant modifications forced the company into bankruptcy.

During the time period since the first practicing of this process, research and development efforts have been common on a worldwide basis. At one time the U.S. BuMines proposed and piloted a process. Perhaps the most important conclusion to be drawn from all these investigations is that the investigators have all applied the same chemistry, but have used various types of reaction vessels in an attempt to achieve economic success. Present day interest in catalystic methods to reduce operating temperatures, lower energy requirements, shorten reactor residence times, and achieve higher process yields may open the door to the development of an economical processing scheme.

Considering the complexity of the process scheme required to produce elemental sulphur, it is not surprising that commercial development took the approach shown by the following reaction:

$$2CaSO_{A} + C \longrightarrow 2CaO + CO_{2} + 2SO_{2}$$
 (5)

While this is the basic reaction employed, initial commercial application was directed toward producing SO₂ for sulphuric acid manufacture and cement as the solid product, Cement formation is accomplished by adding quantities of other raw materials to the gypsum carbon mixture before it is calcined. By varying the composition of the raw material charge, it is possible to produce lime, cement, aggregate-type materials, or even lime-aggregate mixtures.

The cement-sulphuric acid approach was relatively widely adopted in Europe starting in the 1920's with a most successful operation by Marchon in England where natural gypsum was used as a raw material. The situation in England at that time is typical of all cases where this process has been used and can be summarized as follows:

(1) Marchon needed sulphuric acid to support other chemical operations.

(2) The British government limited sulphur imports due to a balance of payment problem and refused to allow additional sulphur imports to satisfy Marchon's growing requirements.

(3) Marchon had large reserves of gypsum, and coal was locally available at attractive prices.

(4) "Home"-produced chemicals would be protected by duties on imported chemicals.

(5) Due to these outside factors affecting their economics, Marchon was able to profitably produce sulphuric acid and cement from gypsum

To date, this process has not been able to "stand alone" when the alternative was to burn sulphur to produce sulphuric acid without help from economic forces outside of those normally used to evaluate the merits of a chemical process. This situation is unchanged today for the gypsum based sulphuric acid-cement plants operating in both South Africa and Poland.

While most of the commercial gypsum processing plants have used natural gypsum as a raw material, phosphogypsum recycling has been a goal of wet process phosphoric acid producers since the first phosphoric acid plants were built. Not having to purchase sulphur has been, and still is, tremendously attractive.

Impurities in phosphogypsum, primarily fluorine and phosphates, complicate its use in any of the thermal processing schemes, but do not disqualify it from being used as a raw material. The plant in South Africa uses 100% phosphogypsum as a feed stock, and the Polish plants are said to use a mixture of natural gypsum and phosphogypsum

Interest in gypsum thermal processing peaked in this country in the 1960's with numerous variations of these processing schemes promoted by various engineering firms, However, the best known work of that time was done by Dr. Wheelock of the University of Iowa. Dr. Wheelock developed a patented process utilizing a fluid bed reactor and using natural gas as both reactive carbon and fuel source. The idea was to use Iowa natural gypsum to produce sulphuric acid and lime, two of the most widely used industrial chemicals, and thereby create a chemical industry in Iowa, While Dr. Wheelock's process was a technical success, it was not economically competitive with sulphuric acid mnde by burning sulphur and/or lime mnde by calcining limestone.

The primary economic shortcomings of this process were the same as for all of the other gypsum thermal processing schemes that had been proposed to that date, namely:

(1) High fuel usage. Fuel is used as a source of both reactive carbon and as a source of energy to raise the materials to reaction temperature.

(2) High capital cost of the plant. These processes are complicated and large-sized reaction vessels are required. Their size and complexity make a gypsum based sulphuric acid-cement plant much more difficult to operate than either a sulphur burning sulphuric acid plant or a limestone based cement plant.

While these two cost factors have dictated economic results, in recent years the capital cost for the plant has perhaps become more critical than the fuel cost.

<u>Institute Programs</u>. One of the first thermal processes investigated under an Institute grant was the production of a high-quality alite type cement from phosphogypsum and phosphatic tailings sand. SO₂ would have been produced as a by-product for conversion to sulphuric acid, The process was not successful in that it was not possible to obtain the high-quality cement product.

With the funding of "Gypsum By-Product Exploitation," the Institute embarked on a thermal process development program that continues today. This proposal was expected to evaluate all recognized uses for phosphogypsum and recommend a course of investigation. However, the primary efforts were directed toward a comparison between two thermal processes:

- (1) OSW Krupp process for producing cement and sulphuric acid.
- (2) Iowa State University (ISU) fluid bed process for producing line and sulphuric acid.

The economic analysis generated in this study indicated that the ISU process was superior to the OSW Krupp process and that it should be possible to utilize this fluid bed method to treat phosphogypsum The proposal recommended that the ISU process be piloted using phosphogypsum to develop data that could be used to more accurately evaluate the economic potential of this process.

This led to the funding of a second proposal, "Gypsum By-Product Exploitation, Phase II, Technical Development of the ISU Process." While a number of processing variables were investigated, the final processing scheme consisted of the following major steps:

(1) **Phosphogypsum washing and clean-up.**

(2) Pelletizing the phosphogypsum While the original pellets were pure phosphogypsum, experimentation demonstrated that the necessary reactive carbon, supplied as coal, could be combined with the phosphogypsum in the pellet. This approach permitted the use of a low-cost, fuel-carbon source such as coal and pointed out that the phosphogypsum coal mixtures were in many ways superior to pure phosphogypsum pellets in a fluidized bed reactor. The pellets used in this process must be uniformly sized by screening. The oversized granules are crushed and mixed with the fines and returned to the pelletizer.

(3) Drying the pellets. Two processing schemes were investigated:

A. Drying before forming the pellets.

- B. Drying after forming the pellets,
- (4) Fluid bed thermal decomposition of the phosphogypsum
- (5) Cleaning and washing of the SO_2 rich exhaust gas stream
- (6) Production of sulphuric acid from the cleaned SO_2 rich gas stream
- (7) Recovery of the solid line product from the fluid bed.

The pilot plant operations were successful in that a satisfactory lime product was generated and the SO₂ content of the exhaust gas stream was high enough to meet the requirements for sulphuric acid manufacture.

Economic analysis based on estimated capital and operating costs were disappointing but they did highlight the two primary cost "problem' areas:

- (1) Capital cost
- (2) Fuel (energy and reactive carbon) cost.

It was recommended that no more work be done with the ISU pilot plant, but that studies that would investigate these two cost problems should be made. In addition, it was pointed out that assigning a value to the solid by-product lime could make this process economically successful and that efforts should be initiated to develop high-volume end uses for the solid by-product.

The next step in this program was "A Proposal for the Recovery of By-Product Gypsum' from Davy-McKee. This proposal was funded to investigate the potential of the rotary grate as a reactor for thermal treatment. It was felt that the rotary grate would have a lower unit capital cost than the fluid bed and that it could achieve lower operating costs. One of the more obvious cost savings was in the elimination of the phosphogypsum washing and clean-up by feeding the raw materials directly to the sizing step. Processing is as follows:

(1) Granule formation. While an attempt is made to produce a "sized" granule, all granules are used and a closely-sized uniform product is not essential.

- (2) Granule drying.
- (3) Circular grate thermal decomposition of the phosphogypsum
- (4) Cleaning and washing of the SO_2 rich exhaust gases.
- (5) Production of sulphuric acid.
- (6) Recovery of the solid line product.

The pilot work completed under this proposal was encouraging and appeared to point the way toward achieving an economical process for recovering the sulphur values in the phosphogypsum It was recommended that additional work be done to determine if the apparent potential benefits of this process could be realized.

The second proposal from Davy McKee, "Phosphogypsum Conversion via Circular Grate Technology," continued the development work initiated in the original proposal. This project confirmed the possibility of achieving much higher production rates than originally thought possible. The process was also modified to eliminate one processing step to give this processing scheme:

- (1) Granule formation.
- (2) Granule drying and thermal decomposition of the phosphogypsum on the circular grate.
- (3) Cleaning and washing of gas stream
- (4) Production of sulphuric acid.
- (5) Recovery of the solid by-product.

This proposal also looked at an alternate solid by-product, an aggregate material. By adding other raw materials it is possible to still release SO_2 and produce a solid rock-like material that could be used for aggregate in concrete or asphalt. While the material generated during the test runs did not totally live up to expectations, additional literature review has suggested ways to overcome the aggregate shortcomings. This proposal will prepare a detailed capital and operating cost estimate. This estimate will be accurate enough that it can be used as a benchmark to compare against other thermal processes.

The question of aggregate production could have far reaching implications. The U.S. BuMines has forecasted that Florida will be importing all its aggregate materials by the year 2,000. If a credit can be taken for a salable solid by-product, the Davy process offers a substantial return on investment.

This process has received some very thorough analysis. Massachusetts Institute of Technology had developed a computer program called "Aspen" for the Department of Energy. This program analyzes chemical unit operations and determines optimum conditions for each processing step. Davy's use of this program has been very helpful and it has resulted in some substantial cost savings in the plant design and operation. This proposal is not completed and everything is encouraging to date.

The next step in thermal processing investigations occurred when a proposal by Science Applications International Corporation, "Conceptual Design and Testing of a Phosphogypsum Reactor" was funded, This project is to develop a "small particle reactor" that would achieve even greater reductions of capital and operating costs. This concept calls for taking phosphogypsum directly from the plant (or pile) and subjecting it to a short duration (seconds) thermal processing. The advantages of this approach can be readily seen when the processing steps listed below are compared to those required for the Iowa State process.

- (1) Thermal decomposition of phosphogypsum crystals in a modified fluid bed.
- (2) Cleaning and washing of the SO_2 gas stream
- (3) Sulphuric acid production.
- (4) Recovery of the solid by-product.

To date, the bench testing has demonstrated that this approach is practical. Conversion in seconds has been accomplished. Additional testing is required and is going forward. While this process is a long way from commercialization, it does show promise.

The most recent thermal processing approach funded was by the U.S. BuMines. This processing route is quite different than that most often proposed and will produce elemental sulphur as a final product. In this case, thermal processing will produce solid CaS rather than SO_2 . The CaS will be subjected to additional processing, primarily in aqueous media, to give a sulphur final product. Progress to date has been encouraging with all chemical reaction routes proven. Future work is intended to improve yields of the various processing steps.

Other Chemical Processes

<u>Background</u>. Phosphogypsum has also been used as a raw material in one non-thermal chemical process, the manufacture of ammonium sulphate according to the following reaction:

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

While this reaction is still employed in plants operating in India, by-product ammonium sulphate from other sources has made this processing approach economically unattractive in most countries.

By substituting other cations for the annonium ion, it is possible to produce other sulphate salts by this chemistry. To date, such production has not proven economically attractive, but it is possible that changing circumstances will favor this approach in the future.

<u>Institute Programs.</u> The Institute has not sponsored research in this area.

Microbiological Processing

<u>Background.</u> It has long been recognized that bacteria can decompose sulphur containing materials and generate H_2S , the familiar rotten egg smell associated with the anaerobic decomposition of both organic and inorganic sulphur containing materials. This type of decomposition occurs on a large scale in every properly operated sewage treatment plant.

There are two requirements for this decomposition reaction:

- (1) Energy
- (2) Organic matter.

In nature the energy is from the sun and the organic matter is derived from animal and/or plant materials. Where inorganic sulphur containing materials are decomposed in this manner, an organic carbon source-frequently equal in weight to the inorganic sulphur material must be available if bacterial action is to take place. A location like Florida, with its abundant sunlight-energy supply would be ideally suited for this type of processing if adequate organic material could be made available. Due to the relatively low rates of production per volume of reaction media, this manner of phosphogypsum decomposition has not been practiced commercially to date.

<u>Institute Programs</u>, The first microbiological project funded would have produced H_2S by bacterial action and converted the H_2S into hydrogen and sulphur by chemical reactions. The proposal was funded in two phases, the first phase to develop a detailed plan of investigation and economic analysis of the processing scheme and the second phase to perform laboratory experimentation to prove the reaction routes selected. After the first phase was completed it appeared that this approach could not have practical application and funding for the second phase was withdrawn.

The second project that was funded (now ongoing) will utilize two different bacterial processes to convert phosphogypsum into sulphur. In this process one group of bacteria will consume organic matter and phosphogypsum to generate H_2S and the second group will convert the H_2S to sulphur. This project is too new to report on its progress.

Agricultural Applications

<u>Background</u>. The agricultural uses for gypsum (from any source) are almost without limit. Phosphogypsum is a superior soil amendment for many soil types and is an excellent fertilizer source of sulphur and calcium Some of the uses discussed here have been well-known for years and have received wide application where soil conditions and economics dictated phosphogypsum utilization.

<u>Soil Amendments.</u> Phosphogypsum has long been used to prepare sodic soils for agricultural purposes and/or to prevent soils from becoming sodic where irrigation waters contain small quantities of salt. For example, phosphogypsum would be an excellent soil treatment for soils reclaimed from the sea in the Netherlands. However, phosphogypsum has probably been more widely used on sodic soils in more arid regions where large-scale irrigation is practiced such as in Israel and some areas in the western United States. Phosphogypsum speeds up the leaching of salt from the soil.

While sodic soils often tend to surface-harden and resist water penetration, this condition can exist in other soil types, particularly high clay content soils. The addition of phosphogypsum to these soils creates a nore open porous soil texture that tends to soak up rainfall rather than just having the water run off the surface and erode the soil. While this effect has been demonstrated on certain soils, it has not received as widespread application as sodic soil treatments. It is also possible to use gypsum to reduce the concentration of other metal ions in the soil, either by a fixation mechanism or by promoting conditions that favor leaching of these ions from the soils, This property of phosphogypsum is particularly valuable where farming and/or fertilization practices have resulted in toxic (to the plants) levels of ions in the soil.

<u>Fertilizer</u>. It has long been recognized that sulphur is almost, if not equally, as essential for proper plant growth as nitrogen, phosphorus and potassium However, the importance of the need to fertilize with sulphur was not a matter of concern as long as animal manures and low-analysis fertilizer were in common use. In addition, coal burning for either home heating or commercial power generation provided additional soil sulphur.

Phosphogypsum is an ideal sulphur source, It is slightly soluble in water and therefore long-lasting in the soil. The sulphur is present in the sulphate form and can be utilized directly by the plant. It is neutral in its soil reactions and does not change the soil pH. And as an added bonus, it contains calcium that is also readily available to the growing plant. While there are many other fertilizer sulphur sources, none of them have all the agronomic advantages of phosphogypsum Elemental sulphur must undergo bacterial conversion to sulphate before the plant can use it. Organic sources of sulphur must be decomposed bacterially before the plant can use the sulphur. While both sulphur and organic sulphur are long-lasting, phosphogypsum demonstrates the same desirable characteristic due to its low solubility. Most of the other sulphate salts that are used for fertilizer are very soluble and the sulphate may be leached from the soil before the plant can use it.

Phosphogypsum does have one major problem as a fertilizer - it is generally available as a wet salt that does not have good handling properties in fertilizer application equipment. If dried, there would be no handling problem but the cost of drying is relatively high. Nevertheless, large quantities of phosphogypsum were shipped from central Florida to south Georgia for peanut fertilization for many years. Peanuts are unique in their high requirement for both calcium and sulphur. Since a phosphate complex was placed in operation in north Florida, most of the phosphogypsum has been supplied by that plant because of the lower freight costs from that facility to the peanut farms.

<u>Institute programs</u>. The Institute has experienced increasing interest by investigators in phosphogypsum in agriculture. While provisions have been made in a number of proposals to determine the fate of the radionuclides found in phosphogypsum, this question has not been considered of significant concern to rule out testing the specific agricultural uses for phosphogypsum that are being studied.

Projects now under investigation will address the following problem areas:

(1) One major problem that is common to all areas of the world is erosion and loss of top soil due to water runoff when the soil does not readily retain rainwater, One common cause of this problem is crusting over of the soil surface as it dries in the sun. This condition can even occur in soils that are primarily sand. When this happens, it is not uncommon to experience top soil erosion due to runoff because the water does not penetrate the soil crust rapidly enough. Phosphogypsum additions to the soil will be evaluated to determine if it is possible to improve physical properties (density, porosity, stability, etc.) of southeastern soils, thereby increasing the water infiltration rate and reducing erosion causing runoff. If the goals of this proposal are achieved, it could have a major impact on crop water utilization in the southeast where short heavy downpours are more common than lengthy light rains where there is little or no surface runoff.

(2) Certain low pH soils in the southeast are very high in soluble aluminum to the point where the soluble aluminum content reaches a level that is toxic to root development in the affected strata. This condition most often occurs in stratas below the surface strata and restricts root growth to the surface or upper stratas. Liming to a higher pH will correct the problem if the lime can be adequately mixed with the affected strata. Accomplishing adequate mixing can be quite difficult where as much as a six-foot deep layer Phosphogypsum applications to the soil surface of soil requires treatment. tend to promote soluble aluminum movement down through the soil and out of the root zone as phosphogypsum saturated rainwater percolates down the soil While the process is lengthy, often requiring several years, it colum. offers a permanent correction to a difficult problem Our five-year project will determine the optimum treatments and measure the effect of treatment on a number of southeastern soils.

(3) It has been proposed that the addition of phosphogypsum to soils devoted to citrus culture will promote the development of a healthier and more disease-resistant root system for the trees planted on the amended soils. It is also expected that the treated soils will result in improved tree nutrition. If these goals can be demonstrated in the project that recently got underway, it could have a tremendous impact upon the Florida citrus industry.

(4) The question of the optimum micronutrient balance for a given crop has become even more critical in these days of high yields and more intense farming to obtain maximum production at the lowest possible cost. Where a micronutrient requirement is at a very low level, it is often difficult to accurately distribute the necessary small quantities of material over the Since all crops require both sulphur and calcium, a proposal has been field. funded to investigate the use of phosphogypsum enriched with the necessary micronutrients as a soil amendment. In this manner, the "carrier" for the micronutrients will not be an inert material but will have definite fertilizer These amendment mixtures will make it possible to add calcium to the value. soil without having the pH problems that have become so common where long-time soil liming has been practiced. In addition, there are no adverse agronomic effects from adding too much phosphogypsum, and the relatively large volume of material that will be applied per acre makes it easier to obtain a uniform distribution of all the micronutrient elements required.

Discussions with other investigators have resulted in the submission of two additional proposals that are now in the review process. The first proposal would look at phosphogypsum fertilization of forage crops with emphasis on the quality of the forage and the results that would be expected when the phosphogypsum fertilized forage is used for animal feed. The second proposal addresses the use of phosphogypsum to supply the sulphur requirements of sugarcane.

Construction Materials

<u>Background</u>. While gypsum has been used as a building material for hundreds of years, phosphogypsum was not seriously considered for this purpose until well into this century. The driving forces for this utilization were two fold and in general both conditions were required before phosphogypsum utilization became common:

(1) Lack of and/or high cost of natural gypsum

(2) Disposal problems for and/or high cost to dispose of phosphogypsum

Where these conditions existed, phosphogypsum utilization in cement, wall board, and other building materials became the rule, Japan is perhaps most typical - a land where natural gypsum is not available and there are severe limits on space for phosphogypsum storage. The pressure to use phosphogypsum was great enough so that new phosphoric acid production processes (hemi-hydrate) were developed that would generate a less contaminated gypsum than that obtained from conventional dihydrate processes. Almost all the phosphogypsum produced in Japan finds its way into building materials.

The pressures to utilize phosphogypsum were not as great in most other parts of the world but the economic advantages of using this material promoted the development of numerous processes for building materials in Europe. These processes have found increasing applications as the rules governing phosphogypsum disposal at sea have been modified to gradually rule out this method of disposal. Most of the products produced in Europe are what could be called "conventional" such as wall board, interior building blocks, etc. These applications of phosphogypsum, other by-product gypsum, or natural gypsum has reached such a high stage of development that it is possible to contract with at least one German firm for a wall board (or other products) plant that will use the gypsum from any source.

Determining past phosphogypsum use in road building is more difficult because there has been no reported widespread usage for this purpose. Phosphate industry people have noted that some phosphogypsum was used as fill It is known that when U.S. 41 was four-laned near the Gardinier plant. Brewster Phosphates (American Cyanamid at the time) used phosphogypsum as a road base on a section of the road leading to the Haynsworth mine in the late 1950's or early 1960's. The entire road to the Brewster Fort Lonesome mine also has a phosphogypsum base. More recently CF Chemicals used phosphogypsum for the road base on their mine entrance road. Conversations with local road builders reveal that phosphogypsum has been used in many private paving jobs, for instance, church parking lots, where the phosphogypsum was given to the The major problem with these instances is that no records parking lot owner. were kept of construction methods and no post construction monitoring has been There are without doubt many other roads in this area with a carried out. phosphogypsum base.

Over the past 10-15 years there has been a large amount of interest and experimentation with fly ash and gypsum (recovered from power plant stack scrubbing) mixtures as road bases. The U.S. DOE and Department of Transportation sponsored much of this work. While phosphogypsum was not used, the results are generally applicable to phosphogypsum fly ash mixtures. Dr. Saylack of Texas A&M University working with Mobil, U.S. DOT, Texas DOT, Texas radiation authorities, and local road building contractors is developing a major road building program in the Houston area for phosphogypsum bases for highways (federal, state, and local) parking lots, storage areas, etc. At present, fly ash sources in Florida are limited but this work could well apply to Florida sometime in the future.

<u>Institute Programs</u>. The only Institute funded program to develop building materials is being carried out at the University of Miami. While this multi-year program has looked at some conventional processing, the major part of the research effort has been directed towards phosphogypsum mixture processing that is unique. One of the products that has come out of this work is cement phosphogypsum mixtures that can be used for all types of structural materials. Particular emphasis has been directed toward the development of load bearing walls. While the first years of this project have been largely concerned with the development of engineering data for the various phosphogypsum mixtures, it is expected that some commercially acceptable building products will reach the final development stage in the next few years.

Development of road building mixtures and techniques have also been addressed under the University of Miami program A number of satisfactory mixtures have been developed and a number of them will be field tested under one of two road building projects that have been funded for Polk and Columbia Counties. These projects will incorporate an extensive environmental nonitoring program to confirm the generally held belief that phosphogypsum used in road building does not represent an environmental problem This premise has been accepted by the Texas DOT and our work should provide adequate data for Florida locations.

An earlier funded proposal by the U.S. Bureau of Mines looked at phosphogypsum for:

- (1) A partial replacement for aggregate in asphalt.
- (2) A raw material for aggregate production.
 - A. Fly ash-phosphogypsum mixtures.
 - B. Thermal treatment of phosphogypsum phosphatic clay mixes.

While products were made, they did not meet the Florida DOT standards for such products, Work on the thermal treatment process was limited and the BuMines proposed a more extensive investigation of these products in a follow-up proposal, This project was not funded because the high fuel costs to produce this aggregate made the approach economically unattractive at that time.

Miscellaneous Projects

<u>Institute Programs.</u> One of the first proposals funded was an "International Symposium on Phosphogypsum" The program attracted speakers and participants from all parts of the world. The interest in successful phosphogypsum utilization was obvious and it was equally obvious that no pat solutions to the problem existed. The Institute continues to reap benefits from this program in that we remain in close contact with quite a number of foreign investigators who keep us appraised of the work going on in other parts of the world.

Several years later a "Workshop on By-Products of Phosphate Industries" was held in Miami. This program was intended to attract primarily Florida people who were interested in developing uses for phosphogypsum The program has generated a number of contacts with road building contractors who are very interested in applying the results of our studies to date.

The "Third Seminar on Phosphogypsum" will be held in Tampa in December of this year. It is again intended more for a local audience but the amount of interest expressed by people from other countries is impressive. Several local road builders who are very interested in using phosphogypsum for private roads and parking lots have indicated that they will be attending.

The "Second International Symposium on Phosphogypsum' will be held in Mami in December 1986. Preliminary contacts with both local and foreign personnel indicates that there is at least as great an interest in this type program now as there was several years ago when the first symposium was held. Preliminary indications are that attendance will exceed the attendance for the first symposium