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**PROCEEDINGS OF THE  
THIRD INTERNATIONAL SYMPOSIUM  
ON PHOSPHOGYPSUM  
SUPPLEMENT**



**Organized by  
The University of Miami  
under a grant sponsored by the  
Florida Institute of Phosphate Research  
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**December 1990**

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**FLORIDA INSTITUTE OF PHOSPHATE RESEARCH**



The Florida Institute of Phosphate Research was created in 1978 by the Florida Legislature (Chapter 878.101, Florida Statutes) and empowered to conduct research supportive to the responsible development of the state's phosphate resources. The institute has targeted areas of research responsibility. These are: reclamation alternatives in mining and processing, including wetlands reclamation, phosphogypsum storage areas and phosphatic clay containment areas; methods for more efficient, economical and environmentally balanced phosphate recovery and processing; disposal and utilization of phosphatic clay; and environmental effects involving the health and welfare of the people, including those effects related to radiation and water consumption.

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

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Proceedings  
of the  
Third International Symposium  
on Phosphogypsum

*Sponsored by*  
**FLORIDA INSTITUTE OF PHOSPHATE RESEARCH**

*Organized by*  
**University of Miami**  
*and held at*  
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TABLE OF CONTENTS

Supplement

Address to the Third International Symposium on Phosphogypsum Jeremy A. Craft .....	1
Phosphogypsum Program at the Florida Institute of Phosphate Research G. Michael Lloyd, Jr. ....	3
Yield, <sup>226</sup> Ra Concentration, and Juice Quality of Oranges in Groves Treated With Phosphogypsum and Mined Gypsum D. L. Myhre, H. W. Martin & S. Nemeč.....	11
The Trial Production Results from Demonstration Plant for Production of Ammonium Sulfate from Phosphogypsum Jing-Yu Chen .....	41
Integration and Ecophos Are Key to the Pine Level Project (Supplement) P. H. Peng, C. B. Earl & W. S. Lawton .....	58
Panel Discussion: The Future of Phosphogypsum J. Beretka .....	64
Robert K. H. Ho .....	67

Address to the  
THIRD INTERNATIONAL SYMPOSIUM ON PHOSPHOGYPSUM

Jeremy A. Craft  
December 6, 1990

Dinner speeches are supposed to be light, lively and, most of all, short. I can promise that this will be short.

To set the stage, let me give you some background on my personal views on the state of the world's environment. I have a particular concern for the environment of the earth. It is in serious trouble. The world as we know it is facing its most critical period since our forbearers came down from the trees and began to walk upright.

The emission of greenhouse gases, global warming, man's spread of plant and animal species outside of their native range, overpopulation all pose a threat to life systems as we know them. Massive changes in climate and mass extinctions are the obvious and certain consequences of these abuses of the environment. It is pessimistic, but I think we have entered a period where, in our lifetimes--and certainly within the lifetimes of our children, we will see catastrophic changes in the earth's life support systems and in the species components of life itself.

How does this relate to what we are doing here? I don't mean to trivialize, but this is one person who believes that the environmental consequences of phosphogypsum production, disposal, reuse, and recycling pale in comparison to the environmental problems facing Florida, this nation, and the world.

There is one given fact about phosphogypsum that everyone can take away from here: because of the emotional media attention given to nonmedical sources of radiation, phosphogypsum will remain controversial whether you stack it, spread it, or reprocess it.

This week's" issue of the New England Journal of Medicine reported that doctors who own their own X-ray machines require their patients to take four times as-many X-rays as those doctors that don't own machines. A tremendous profit incentive with a calculable health risk. But where did you find the report of this in the newspaper? Section D of USA Today, next to a picture of and article about Roseanne Barr and her ability or inability to sing.

If that were a story about minor increases in health risks caused by a mining company, it would have been on the front page of virtually every newspaper in Florida. We are allowing the environmental sciences and industrial development of this nation, and indeed the world, to be directed by the twits in the media who can't even get a quote right--much less understand a complex issue. They want sales regardless of scientific merit.

We are being forced to examine environmental issues of minor consequence because NIMBY sells. For those of you unfamiliar with the term, NIMBY means "not in my back yard." NIMBY has become so popular that it has spawned NIMFYE--"not in my front yard either." Of course seeing this, the politicians have become involved with NIMD--"not in my district" and NIEY--"not in election years." This is all leading to NOPE--"not on Planet Earth."

It is amazing that this is occurring on issues like phosphogypsum use in industrialized countries while we enjoy our modern life style. All the while, we turn a blind eye toward tropical deforestation, population growth and the use of US-made chemicals like DDT in third world countries.

Cancer risks from phosphogypsum stacks are being thrown around as 1/10,000 to 1/1,000,000. I don't know which is correct and I won't pretend to tell you which you should believe. But, I do know that we are extrapolating the unlikely based on the improbable using unverifiable hypotheses.

It boggles my mind, especially considering that statistics show that 1 in 10 American women will develop breast cancer in their lifetimes. One-fourth of those will die as a result, and we still don't have a national policy to provide for early detection. I think it is criminal. We are forced to focus on comparatively minor problems like phosphogypsum, yet work on solutions to truly severe problems go unaddressed or under funded.

What does the future hold? I see two things as necessary. One to solve the global problems and the other for phosphogypsum. They both have an equal likelihood of occurrence.

Globally, environmental problems will only be solved if government can develop vision independent of special interest pressures and force the alteration of our present lifestyles in such a way as to reduce the environmental insults generated by our modern, wasteful, high-tech world.

Publicly palatable phosphogypsum solutions will only come when one of you develops a chemical process that alters the laws of thermodynamics resulting in the elimination of the radioactive constituents.

In closing, let me urge all of you to take a holistic view whether you be a researcher, regulator, or producer. Your action, or inaction, has truly global consequences. Consider them in your decision-making and make the responsible move for the benefit of the world and not one individual or one company.

Thank you and good luck in your endeavors.

**PHOSPHOGYPSUM PROGRAM AT THE  
FLORIDA INSTITUTE OF PHOSPHATE RESEARCH**

**G. Michael Lloyd, Jr.  
Florida Institute of Phosphate Research**

**Third International Symposium on Phosphogypsum  
Orlando, Florida  
December 4-7, 1990**



**PHOSPHOGYPSUM PROGRAM AT THE  
FLORIDA INSTITUTE OF PHOSPHATE RESEARCH**

The Florida Institute of Phosphate Research was created by the Florida Legislature in 1979 and instructed to do or cause to be done research that would benefit:

- (1) The phosphate industry,
- (2) The State of Florida, and/or
- (3) The people living in the vicinity of phosphate mining and processing.

At that time there was almost 400 million tons of phosphogypsum stockpiled in Florida and the "Utilization of Phosphogypsum" was given priority status. It is interesting to note that one of the first projects funded by FIPR was the "First International Symposium on Phosphogypsum" that was held at Lake Buena Vista in November 1980.

Since our organization is instructed to do research that has application to present problems we have used the following criteria as guidelines for selecting research programs. Proposals should be:

- (1) Technically feasible,
- (2) Environmentally sound,  
and have the potential to develop:
- (3) A high profit use,  
and/or
- (4) A high volume use.

With this background, the goals of our phosphogypsum program have been to develop the following applications for phosphogypsum

- (1) As a Chemical Raw Material
  - (a) SO<sub>2</sub> production
  - (b) Sulfur production
  - (c) Other products
- (2) As a Construction Material for
  - (a) Road building
  - (b) Building products
- (3) In Agriculture
  - (a) Fertilizer
  - (b) Soil conditioner

With an adequate supply of phosphogypsum on hand, at present on the order of 600 million tons, the high volume uses for phosphogypsum have been of particular interest and have been investigated with the intention of first developing uses that would reduce and eventually eliminate further accumulations and secondly develop additional uses that would contribute to a slow but steady reduction of existing inventories.

The most obvious solution to eliminating further accumulations is to utilize phosphogypsum as a chemical raw material in a process(es) to recycle the sulfur values to produce sulfuric acid for additional phosphoric acid production. The projects listed below were funded to evaluate this type technology:

**ISU Fluid Bed Process**  
**Zellers-Williams, Inc.**

**FIPR 80-01-002**      **Gypsum By-Product Exploitation.** This project evaluated options for phosphogypsum processing and selected the ISU Fluid Bed Process for more detailed study.

**FIPR 80-01-002A**      **Gypsum By-Product Exploitation, Phase II, Technical Development of ISU Process.** Evaluated the fluid bed conversion of phosphogypsum to lime and SO<sub>2</sub>. Pilot plant demonstration of the process used coal as a fuel. Employed a phosphogypsum clean up step.

**Circular Grate Process**  
**Davy McKee Corporation**

**FIPR 81-03-013**      **A Proposal for the Recovery of By-Product Gypsum**

**FIPR 83-01-021R**      **Phosphogypsum Conversion by Circular Grate Technology.**

**FIPR 87-01-071**      **Operation of the Batch Test Unit.** (FIPR) These projects are the basis for the development of a circular grate process to generate SO<sub>2</sub> and an aggregate product that could be used in road building. This project is on-going in that the batch test unit is still being operated to test specific raw materials.

**Small Particle Reactor Process**  
**SAIC**

**FIPR 83-01-027**      **Conceptual Design and Testing of a Phosphogypsum Reactor.**

**FIPR 85-01-040**      **Conceptual Design and Testing of a Phosphogypsum Reactor.**

**FIPR 85-01-042**      **Conceptual Design and Testing of a Phosphogypsum Reactor.**

**FIPR 87-01-072**      **Operation of a Small Particle Test Reactor to Optimize Phosphogypsum to SO<sub>2</sub> Conversion.** This process produced lime and SO<sub>2</sub> at a relatively high SO<sub>2</sub> concentration. Process work has been discontinued due to the high cost of the program required to complete larger scale pilot testing and build and operate a demonstration plant.

Slagging Process  
Science Ventures, Inc.

- FIPR 87-01-055      Sulfur Dioxide Recovery in a Slagging Process.
- FIPR 88-01-077      Sulfur Dioxide Recovery from Phosphogypsum in a Slagging Process. This process operates at a higher temperature than is normal for thermal processing with a high throughput rate and produces a solid product suitable for use as an aggregate material.

Recognizing that there are distinct advantages to recovering sulfur rather than SO<sub>2</sub>, a project by the Bureau of Mines was approved:

- FIPR 84-01-036      Recovery of Sulfur from Phosphogypsum This project employed the classic first step of thermal processing to obtain CaS with a unique sulfur recovery from the CaS.

While interest has been low, two projects to utilize microbiological means to recover sulfur have been initiated:

- FIPR 84-01-039      Conversion of CaSO<sub>4</sub> Wastes to Marketable Products. (Florida Institute of Technology)
- FIPR 84-01-039      Microbial Methods for Sulfur Recovery. (University of Miami)

Both projects had the goal of recovering sulfur with the second project utilizing an all microbial systems.

Phosphogypsum used in construction represents an excellent way to convert a low-value raw material into a high-value product. However, early in the development of our program the fact that Florida phosphogypsum is slightly radioactive had to be considered. Knowing that this had not presented a problem in those areas around the world where phosphogypsum is utilized in building products and determining that the information available in the literature supported such uses, we still elected to limit research on such products due to the public perception that all radioactivity is undesirable. Instead we concentrated our efforts on road building where the volume of material that could be used was potentially high.

Florida is one of the fastest growing states and road building and repair is a major construction activity. In addition, Florida does not have a good local aggregate source and imports much of the material used. The U.S. Bureau of Mines has forecasted that all aggregate would be imported by the year 2000.

Phosphogypsum alone, or phosphogypsum combined with other materials, can be used in road bases for all types of roads from secondary roads with light traffic to primary highways that are subject to very heavy traffic loadings. FIPR has sponsored the construction of two secondary roads, one in Polk County in central Florida and the second in Columbia County in north Florida.

Secondary Road Projects  
University of Miami

- FIPR 84-01-033      Rebuilding a Polk County Road Utilizing a Phosphogypsum Mixture.
- FIPR 85-01-041      Rebuilding a Columbia County Road Utilizing a Phosphogypsum Mixture.
- FIPR 87-05-033R      Environmental Monitoring of Polk and Columbia Counties Experimental Phosphogypsum Roads. (FIPR)

Road building cost comparisons strongly favored the phosphogypsum road bases versus the conventional road base construction.

The most costly, and in the long run perhaps the most valuable aspects of these projects was the inclusion of an environmental monitoring program that covered the period before, during and after construction. At the completion of the original projects it was decided that FIPR would continue the environmental monitoring program for an additional two years. The final testing for this two-year extension has been completed and while all of the samples have not been analyzed at this time, all additional test work has confirmed the conclusions drawn after the first three years, that there are no significant environmental effects associated with using phosphogypsum in road building. It should be noted that FIPR routinely requires an environmental component be included in phosphogypsum projects. While we are satisfied that phosphogypsum can be used without environmental problems or we would not recommend its use, there is relatively little hard data that can be used to demonstrate this fact and this data must be collected and be made available to all concerned parties.

There are other road projects that are worthy of mention:

- FIPR 87-01-068      A Demonstration Project on Roller Compaction Concrete. (University of Miami)
- FIPR 90-01-087      Stabilized Silica-Gypsum Base Heavy Traffic Field Test - Phase I. (Bromwell and Carrier, Inc.)

The roller compaction concrete road demonstrated a technology that is new to this area. Roller compacted concrete forms a very high load bearing surface and the addition of 15% phosphogypsum to the normal mixture makes a substantial improvement to the final road. The stabilized silica-gypsum base will include a small amount of cement in the base mixture. It is intended to demonstrate the effectiveness of a phosphogypsum base under heavy traffic consisting of a large number of large heavily loaded trucks. Unfortunately, this project has been delayed awaiting a final EPA ruling under NESHAP.

While road building has received first priority in the construction area, building products have not been totally ignored. At least 25% of the research under these two projects has been devoted to building materials:

Construction - General  
University of Miami

FIPR 82-01-014      Reclamation, Reconstitution and Reuse of Phosphogypsum Wastes for Building Materials.

FIPR 85-01-044R      Reclamation, Reconstitution and Reuse of Phosphogypsum Wastes for Construction Materials.

Perhaps one of the more interesting things that this research has shown is that radon emissions from the building products can be significantly reduced by both the method of preparation of the building material and the application of a coating such as paint to the interior surfaces of the phosphogypsum products.

Phosphogypsum in agriculture also has the potential to provide an outlet for large quantities of phosphogypsum. Florida soils, like much of the southeastern part of the country, do not contain sulfur at levels that are optimum for plant growth. Phosphogypsum is an almost ideal way to correct these sulfur deficiencies.

Fertilization

FIPR 85-01-048      Phosphogypsum to Increase Yields and Quality of Forage. (Auburn University)

FIPR 89-01-085R      Influence of Phosphogypsum on Forage Yield and Quality in a Typical Florida Soil. (University of Florida)

FIPR 85-03-064      Use of Phosphatic Clay and Phosphogypsum on Citrus Soils. (USDA)

While these uses would be low profit to the phosphogypsum producer, they do offer the opportunity for major benefit to the state's economy. It is not always recognized that Florida is a cattle producing state, rivaling Texas as a cattle grower. It has been shown in studies in various parts of the world that proper sulfur fertilization of grass land can contribute to increased weight gain in livestock grazing on these treated pastures. Increased weight gains as much as 20% have been reported.

Citrus fertilization is another matter. This program utilized phosphogypsum as a calcium source. Phosphogypsum, unlike lime, does not change the soil pH and can be applied routinely to crops that require large quantities of either calcium or sulfur. Repeated applications over many years are possible without the need to take corrective action to maintain the soil pH.

The state of Florida produces large quantities of vegetables and optimum yields are most often dependent upon the crop in question receiving the proper mix of micronutrients at the proper time during the growing season. A project to demonstrate the value of granular phosphogypsum as a micronutrient carrier was conducted.

#### Soil Amendments

**FIPR 84-01-034**      Fortified Phosphogypsum as a Soil Amendment.  
(Agro Services International) One goal of the study was to obtain improved yields but a surprising result with some vegetable crops was the finding that the reduced level of physical blemishes that would not be accepted by customer, equated to a measurable increase in produce that could be sold.

Our part of the country can also benefit from phosphogypsum applied as a soil conditioner as shown by the following projects:

#### Soil Conditioning

**FIPR 83-01-024R**      Gypsum as an Ameliorant for Subsoil Acidity  
(University of Georgia)

**FIPR 83-01-020**      Use of Gypsum to Improve Physical Properties of Southeastern Soils (University of Georgia)

The problem of subsoil acidity and related aluminum toxicity is not an uncommon problem and can occur at various soil depths. With phosphogypsum it is not necessary to plow, sometimes as deep as six feet, to incorporate lime into the acid layer. Surface application of phosphogypsum and rainfall to transport the phosphogypsum down the soil column will correct this condition.

Improved physical properties of soils can be very beneficial in the southeastern states where very heavy short duration rainstorms are common. The use of phosphogypsum modifies the soil structure so that there is more rapid water absorption and less runoff to cause erosion of the soil.

While our primary goal is research, research is of no value if the results of the research, whether it be conducted by FIPR or others, is not made available to others through an ongoing dissemination and exchange of information.

FIPR's practice is to publish the results of the work done under our grants. However, a very critical aspect of the program is accomplished at meetings devoted to phosphogypsum. You will be experiencing one of these meetings over the next few days. The program has included:

### **PhosphogypsumConferences**

<b>International Symposium on Phosphogypsum</b>	<b>1980</b>
<b>Second Workshop on By-Products of Phosphate Industries</b>	<b>1984</b>
<b>Third Workshop on By-Products of Phosphate Industries</b>	<b>1985</b>
<b>Second International Symposium on Phosphogypsum</b>	<b>1986</b>
<b>Third International Symposium on Phosphogypsum</b>	<b>1990</b>

**We would hope that there will be many more opportunities for us to get together to discuss this challenging subject and we look forward to getting to know you better as this symposium continues.**

Yield,  $^{226}\text{Ra}$  Concentration, and Juice Quality of  
Oranges in Groves Treated With Phosphogypsum  
and Mined Gypsum

D.L. Myhre\*, H.W. Martin, and S. Nemeč<sup>1</sup>

ABSTRACT

Phosphogypsum (Pg) is accumulating in stacks in Florida, USA at the annual rate of 30 million tons, adding to the existing accumulation of about 600 million tons. The objectives of this study were to determine if Pg and mined gypsum (MG) applications to soil (South Florida Spodosols) in citrus groves would affect fruit yield, radioactivity in fruit, juice quality, or leaf mineral concentration. Treatments included Pg rates of 0, 560, 1120, and 2240 kg ha<sup>-1</sup>, and a MG rate of 2240 kg ha<sup>-1</sup>, applied to three citrus groves for three years. The effects of soils (including scion/rootstock and cultural management) were more substantial than those of gypsum application. On all soils, Pg had no effect ( $P < 0.05$ ) on fruit yield. However, with Myakka soil, where fruit yields were near the state average, Pg rate effect was quadratic ( $P < 0.10$ ), i.e., maximum yield occurred with 1120 kg ha<sup>-1</sup>. Phosphogypsum had no effect on juice  $^{226}\text{Ra}$  concentration. Phosphogypsum application increased juice Brix with Myakka soil, decreased juice



titratable acidity with Oldsmar soil and across all soils, and increased Brix/acid ratio with Myakka and Oldsmar soils and across all soils. Phosphogypsum increased the Ca concentration of the juice of 'Pineapple' orange [C. sinensis Osb.] but had no effect on juice K concentration. Phosphogypsum increased leaf Ca, decreased leaf Mg and K, and had no effect on leaf N concentrations. In summary, Pg could be applied to Spodosols at a rate up to 2240 kg ha<sup>-1</sup> (1 t A<sup>-1</sup>) annually for three years without significantly (P<0.05) increasing or decreasing yield or <sup>226</sup>Ra concentration of oranges.

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Additional index words

Aluminum toxicity, Brix, soil acidity, Spodosols, calcium, phosphorus, citrus.

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Phosphogypsum (Pg) is a by-product of the production of phosphoric acid from phosphate ore. The Florida Institute of Phosphate Research<sup>2</sup> estimates that approximately 600 million tons of Pg are stockpiled in west-central Florida and over 30 million tons are added annually. Few immediate prospects exist for safe and economical disposal of this material.

Toxic levels of soil Al, sometimes accompanied by deficient levels of Ca, may restrict or entirely prevent root exploration of subsoil horizons (Pearson, 1966). Mined gypsum (MG) and Pg have been considered as soil amendments to ameliorate Al toxicity in the subsoil horizons of some highly weathered soils (Oates and Caldwell, 1985; Bouton et al., 1986; Sumner et al., 1986). Increases in yield of perennial crops such as alfalfa, coffee, peach, and apple have been observed with application of Pg or MG. Such responses generally were sufficient to cover the cost of gypsum within 3 to 4 years (Shainberg et al., 1989). Similar results might be expected with citrus when it is grown on soils with acidic subsoil horizons high in Al and low in Ca. Gypsum and Pg have been applied on one upland soil in Florida (Anderson, 1968) at rates up to 33.3 Mg ha<sup>-1</sup> over 2.5 yr. These rates reduced tree growth, cold

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<sup>2</sup>Personal communication, Gordon Nifong. 1990.

tolerance, and fruit yields of cultivar 'Parson Brown' [C. sinensis (L.) Osb.]/sour orange (C. aurantium L.) and cultivar 'Valencia' [C. sinensis (L.) Osb.]/rough lemon (C. jambhiri Lush.). Lower rates such as 2240 kg ha<sup>-1</sup> had no significant effects (Anderson, 1968).

Spodosols of the Southern Florida Flatwoods Land Resource Area (Caldwell, 1980) are of interest in this regard because land planted to citrus is currently increasing on these soils due to severe freezes in 1981, 1983, 1985, and 1989 (U.S. Dept. Commerce, 1981-1989) that have destroyed thousands of hectares of citrus on the North Central Florida Ridge. In flatwood soils, the rooting volume of citrus may be limited by high water tables. Thus the depth of soil available for root development of citrus trees is much less in Spodosols of the South Florida Flatwoods (Lin, et al., 1987) than in Entisols of the North Central Florida Ridge. Information is needed pertaining to the effects of Pg with Spodosols on citrus yield and juice quality.

The primary naturally-occurring radioactive isotope in most foods is <sup>226</sup>Ra. Studies have been conducted on elevated levels of naturally-occurring radioactivity (<sup>226</sup>Ra) in food grown on reclaimed phosphate mined land (Guidry, 1985). Other studies have examined the radiation problems associated with phosphate ore-mining wastes including Pg (Guimond and Windham, 1979; USEPA, 1973) and mined

agricultural gypsums (Lindenken and Coles, 1977). Phosphogypsum produced in Central Florida contains an average of 26 pCi  $^{226}\text{Ra}$   $\text{g}^{-1}$  (Roessler et al., 1979). The application of Pg to soil used for citrus production in Florida has been examined for the purposes of disposing of this material on Entisols (Anderson, 1968) and ameliorating Al toxicity in the subsoil horizons of Spodosols (Martin et al., 1987; Lin et al., 1987). Information is needed on the effects of soil Pg application on  $^{226}\text{Ra}$  content of citrus fruit.

The objectives of this study were to determine if Pg and MG applications to soil in citrus groves would affect fruit yield, radioactivity in fruit, juice quality, or leaf mineral concentration on typical South Florida Spodosols. That part of the field study involving gypsum effects on subsoil chemical properties will be described elsewhere (Myhre and Martin, 1991).

## MATERIALS AND METHODS

### Grove Sites and Experimental Design

Three mature citrus groves in the South Florida flatwoods were selected to represent three soil series, each with different depths to the Bh spodic horizon. These soils included Myakka (Aeric Haplaquod) and Smyrna (Aeric Haplaquod) fine sands, and Oldsmar fine sand (Alfic Arenic Haplaquod). The Bh horizons are within the depths of >50

cm, 100-170 cm, and < 50 cm for Myakka, Oldsmar, and Smyrna respectively. The Bh of the Oldsmar soil is underlain by a Bt clay horizon (Myhre, et al., 1987). These Spodosols were selected because of a substantial hectarage of citrus currently grown on each of them in Florida. Also, previous studies (Myhre et al., 1987) described the contents of extractable nutrients and potential reactive Al in horizons of the same three soils.

Citrus trees grown on Myakka soil were 'Pineapple' orange (Citrus sinensis (L.) Osb.) on Cleopatra mandarin (C. reticulata L.) rootstock planted in 1965 at 369 trees ha<sup>-1</sup>. Trees grown on Oldsmar soil were 'Hamlin' (C. sinensis (L.) Osb.) on Cleopatra mandarin rootstock planted in 1961 at 252 trees ha<sup>-1</sup>. Trees grown on Smyrna soil were 'Hamlin' on sour orange (C. aurantium L.) rootstock planted in 1966 at 308 trees ha<sup>-1</sup>. Tree spacings within rows were 3.7, 5.0, and 3.8 m and bed widths were 14.6, 15.9, and 8.8 m in Myakka (1 row/bed), and Oldsmar and Smyrna (2 rows/bed) soil sites, respectively. All groves received about the same annual amount of fertilizer (kg ha<sup>-1</sup>), 220 N, 13 P, 185 K, 15 Mg, and a small amount of B. Nutritional foliar sprays of Cu, Zn, and Mn were applied based on annual grove inspections. Irrigation was provided by overhead sprinklers on the Smyrna soil, and subsurface irrigation on the other two soils.

A randomized complete block design was used with four blocks (replications), each with five treatments. Each of the 20 total plots on each of the three soils contained eight trees with guard trees on all sides. All of the trees started from an "equal health" standpoint at the beginning of the experiment. Treatments included Pg rates of 0, 560, 1120, and 2240 kg ha<sup>-1</sup>, and a MG rate of 2240 kg ha<sup>-1</sup>, applied broadcast by hand each year in March the first two years (1986, 1987) and July the third year (1988). The Pg and MG were analyzed for Ca, S, P, F, and Al (ASTM Committee C-11, 1985).

#### Crop Parameters

The yield of oranges was determined in the third year. Fruit grown on Oldsmar soil was harvested 27 Dec., 1988, on Smyrna soil 3 Jan., 1989, and on Myakka soil 10 Jan., 1989. Fruit was harvested from the four center trees in each eight-tree plot and composited into field boxes with a capacity of ten 41 kg (90-lb) boxes of fruit. Yield of oranges was estimated for each plot and converted from kg tree<sup>-1</sup> to Mg ha<sup>-1</sup>.

The <sup>226</sup>Ra concentration of the fruit juice was measured in December 1986 and 1988 from a composite sample of 40 oranges (10 from the outside of each of four center trees per plot). The <sup>226</sup>Ra in juice was concentrated by precipitation with BaSO<sub>4</sub>, further processed, and alpha

scintillations were counted using a photomultiplier tube by the method of Osmond et al. (1984).

Quality of fruit juice was estimated from samples of 20 oranges harvested from the outside portion on all sides (north, south, east, and west) of each of the four center trees in each plot. Fruit was refrigerated until analyzed for Brix, titratable acidity, and mineral concentration of juice.

Fruit samples were brought to room temperature (25 °C) and squeezed. After straining the juice, readings of Brix (total soluble solids) were obtained with a refractometer (Wardowski et al., 1979). Refractive index expressed in terms of pure sucrose, was measured with a few drops of juice. A sample of juice was titrated with NaOH (Wardowski et al., 1979) to measure titratable acidity. The Brix/acid ratio was calculated.

Juice mineral concentrations were measured only with 'Pineapple' orange fruit harvested from trees grown on Myakka soil. A 25-g aliquot of juice was placed in a porcelain dish, evaporated to dryness, and placed in a furnace at 550 °C for 2 h. Ash was dissolved in a few mL of HCl and diluted to a final volume of 50 mL in 0.1 M HCl. Measurements were made of Ca, K, Mg, P, Mn, and Zn concentrations using an ICAP spectrometer.

Leaf samples from non-fruiting twigs were collected on June 22, 11, and 23, 1989 from trees on Myakka, Oldsmar, and

Smyrna soils, respectively. They were individually and thoroughly washed with a detergent solution, rinsed in distilled water, air dried, and ground in a Wiley mill (Koo et al., 1984). Two-gram samples were digested by the Kjeldahl method for total nitrogen analysis (Nelson and Sommers, 1980). For mineral analysis, ground samples were ashed at 550 °C for 2 h. Ash was dissolved in a few mL of HCl, diluted to a final volume of 50 mL in 0.1 M HCl, and analyzed on an ICAP spectrometer for Ca, K, Mg, and P concentrations.

#### Statistical Analysis of Data

Single degree of freedom contrasts (SAS Institute, 1985) were used to compare data means from the four Pg rates, the three soils used, and Pg vs. MG at the 2240 kg ha<sup>-1</sup> rate. Regression analysis (SAS Institute, 1985) was used to evaluate the simultaneous variation of Pg rate and the various dependent variables. Significant contrasts were shown at the lowest level of probability possible (0.10, 0.05, 0.01, or 0.001 %).

### RESULTS

Phosphogypsum and mined gypsum. The Pg was 22.21% Ca, 16.59% S, 0.32% P, 0.48% F, and 0.07% Al. The MG was 22.82% Ca, 16.38% S, 0.03% P, 0.03% F, and 0.09% Al. The remainder for both materials consisted of bound oxygen, free water,



and impurities . The pH's of the Pg and Mg were 4.7 and 7.8, respectively.

Fruit yields. The effects of soils (including scion/rootstock and cultural management) were more substantial than those of gypsum application (Fig-1). Highest yields were produced on Smyrna soils by 'Hamlin'/sour orange trees.

The Florida Agricultural Statistics Service (1989) reported that average orange production was 41 Mg ha<sup>-1</sup> (407 90-lb. boxes A<sup>-1</sup>) in South Florida for the 1988-89 season. Production on the Myakka soil was similar to the industry average, but production was higher on the other two soils. On Myakka soil, Pg rate had a quadratic effect (P<0.10) on fruit yield (Fig. 1) with the highest yield (51.3 Mg ha<sup>-1</sup>) occurring with 1120 kg ha<sup>-1</sup> Pg. Yields were similar with Pg and MG. Yields on Smyrna and Oldsmar soils were not influenced by Pg or MG. The standard deviations (SD) of the yield data (Fig.1) show considerable variability between replicates of the same treatment. Such variation is not uncommon. With fruit yield and other dependent variables, regression equations were characterized by very low r<sup>2</sup> values. Thus, they are not shown because single degree of freedom contrasts provided more meaningful descriptions of treatment effects.

Juice  $^{226}\text{Ra}$  concentration. All of the values were relatively low. The highest fruit juice  $^{226}\text{Ra}$  concentration observed in an individual sample was 3.0 pCi L<sup>-1</sup> (data not shown) while the highest mean concentration was 1.72 pCi L<sup>-1</sup> (Fig. 2). Juice from fruit grown on Myakka soil was observed to have the highest overall mean  $^{226}\text{Ra}$  concentration at 1.22 pCi L<sup>-1</sup> vs. 0.52 pCi L<sup>-1</sup> on Oldsmar (Fig. 2) and 0.69 pCi L<sup>-1</sup> on Smyrna soils (Fig. 2). On Myakka and Oldsmar soils, mean  $^{226}\text{Ra}$  concentrations were not influenced by year or Pg rate. On Smyrna soil, (Fig. 2) Pg rate had no effect on  $^{226}\text{Ra}$  concentration, but year effect was highly significant ( $P < 0.001$ ) with an average  $^{226}\text{Ra}$  concentration of 0.47 pCi L<sup>-1</sup> in 1986 and 0.92 pCi L<sup>-1</sup> in 1988.

Juice quality. On Myakka soil, orange juice Brix values (Table 1) increased linearly with increases in Pg rate. On Myakka soil, Brix value was higher with Pg (14.0) than with MG (13.3) with the 2240 kg ha<sup>-1</sup> gypsum rate. Juice Brix values of fruit grown on Smyrna and Oldsmar soils were not influenced by gypsum.

On Oldsmar soil, juice acid percentage (Table 2) decreased linearly with increases in Pg rate. Juice acid percentage values were similar with Pg and MG.

Juice Brix/acid ratio values (Table 3) increased linearly with increases in rate of Pg applied to Oldsmar and Myakka soils. Brix/acid ratio values were similar with Pg

and MG. Juice Brix/acid ratio values of fruit grown on Smyrna soil were not influenced by gypsum.

Juice mineral concentrations. Values for elemental composition of orange juice from trees treated and not treated with Pg fall within the range of reported values for orange juice (McHard et al., 1980). Calcium and Mn concentration in juice from 'Pineapple' oranges grown on Myakka soil (Table 4), increased linearly with increases in Pg rate. Magnesium, K, P, and Zn concentrations in juice were not influenced by gypsum rate or type.

Leaf mineral concentrations. On Myakka soil (Table 5), pg rate effect on leaf magnesium concentration was quadratic. The lowest leaf magnesium concentration ( $3.3 \text{ g kg}^{-1}$ ) was observed with  $2240 \text{ kg ha}^{-1}$  Pg. Leaf P concentration was influenced by a quadratic Pg rate effect.

On Oldsmar soil (Table 6), leaf Ca concentration increased linearly with increases in Pg rate. Leaf Mg concentration decreased linearly with increases in Pg rate. Leaf P concentration increased linearly with increases in Pg rate.

On Smyrna soil (Table 7), leaf Ca was increased linearly with increases in Pg rate. Leaf K concentration was higher with MG ( $13.6 \text{ g kg}^{-1}$ ) than with Pg ( $12.9 \text{ g kg}^{-1}$ ). Leaf Mg concentration was influenced by a quadratic Pg rate

effect. The maximum Mg concentration ( $4.3 \text{ g kg}^{-1}$ ) occurred with  $560 \text{ kg ha}^{-1}$  Pg.

Phosphogypsum rate did not influence leaf K concentration on any one soil. When data from all soils/locations were analyzed together, however, increases in Pg rate resulted in a linear decrease (data not shown) in leaf K concentration from  $17.4$  to  $16.2 \text{ g kg}^{-1}$ . Gypsum had no effects on leaf N concentrations which averaged  $27 \text{ g kg}^{-1}$  (data not shown).

In summary, after three Pg applications ( $2240 \text{ kg ha}^{-1} \text{ yr}^{-1}$ ) on three soils, Pg, compared to the check treatment, increased leaf Ca concentration 8%, and decreased leaf Mg and K 1.5 and 7%, respectively. However, both Mg and K concentrations were in the optimum range (Koo et al., 1984).

#### DISCUSSION AND CONCLUSIONS

On Myakka soil where 'Pineapple' orange yields were approximately equal to the state average, fruit yield increased with increases in Pg rate up  $1120 \text{ kg ha}^{-1}$ . A further increase in Pg rate resulted in a decrease in yield. These data along with those of Anderson (1968) indicate that Pg applied at annual rates higher than  $2240 \text{ kg ha}^{-1}$  can be detrimental to citrus grown on some sandy Florida soils. Phosphogypsum rates of  $1120 \text{ kg ha}^{-1}$  or less, however, can be beneficial to citrus grown on some sandy Florida soils. Responses to this rate were consistent with those observed

with other crop species in Georgia, USA and South Africa (Shainberg et al., 1989).

Phosphogypsum application had no effect on juice  $^{226}\text{Ra}$  concentration. The data of Guidry (1985) showed that  $^{226}\text{Ra}$  concentrations of oranges averaged  $1.65 \text{ pCi L}^{-1}$  when produced on un-mined land and  $4.24 \text{ pCi L}^{-1}$  when produced on reclaimed phosphate mine land. For even the highest Pg rates applied in this study, fruit juice  $^{226}\text{Ra}$  concentration means were no more than "background levels" observed by Guidry (1985).

Phosphogypsum application increased juice Brix with Myakka soil, decreased juice titratable acidity with Oldsmar soil, and increased Brix/acid ratio with Myakka and Oldsmar soils. This ratio is a measure of the balance of sugar to acid and, thus the palatability of the juice. Hence, when sugars are low, acid must be proportionally low as well if palatability is to remain good (Krezdorn, A.H., 1978; Wardowski et al., 1979). All Brix and Brix/acid ratio values observed in this study were within ranges considered adequate (Whiteaker, 1988).

Phosphogypsum application increased the Ca and Mn concentrations of the juice. Though the increase in juice Ca concentration with increases in Pg rate was significant, it may not be of practical significance for human nutrition due to the small quantities involved. Other workers have observed increases in plant Mn and Ca uptake as a result of

gypsum application. These workers did not explain why Mn uptake should increase along with Ca uptake when increased Ca uptake would be expected to decrease Mn uptake by plants (Foy, 1984; Shainberg et al., 1989). One of the most important orange juice minerals for human nutrition is K. Concentrations of juice K were not affected by Pg or Mg application.

Phosphogypsum resulted in increased concentration of Ca in leaves of citrus trees grown on two of three soils (Oldsmar and Smyrna). Leaf K was decreased slightly. Leaf Mg concentration was decreased by the 2240 kg ha<sup>-1</sup> Pg rate with all soils, but was still within the optimum range (Koo et al., 1984). Such increases in leaf and juice Ca and decreases in leaf K and Mg are consistent with observations of other workers (Shainberg et al., 1989). These statistically significant effects had, however, no practical biological significance. Souza and Ritchey (1986) found that gypsum application increased root development thus increasing NO<sub>3</sub><sup>-</sup> recovery from subsoil horizons by other crop species. In our study, however, gypsum had no effects on leaf N concentration. All observed leaf N, Ca, K, and Mg concentrations were within optimum ranges (Koo et al., 1984). With the one soil (Smyrna) on which leaf P concentrations were increased by Pg, concentrations were in the low end of the optimum range, (Koo et al., 1984).

Shainberg et al. (1989) found recorded in the literature no meaningful differences between Pg and MG in their effects on crop response to gypsum. In our study, Pg and MG were compared at an application rate of 2240 kg ha<sup>-1</sup>. Phosphogypsum resulted in higher juice Brix values than did MG on one soil. Mined gypsum resulted in higher leaf K concentrations on one soil. In several instances, while 1120 kg ha<sup>-1</sup> Pg was beneficial to citrus, 2240 kg ha<sup>-1</sup> was detrimental. Some differences between the effects of the two types of gypsum may have been due to the greater solubility of Pg, as opposed to MG (Keren and Shainberg, 1981). Future studies comparing effects of the two gypsum sources could use annual rates lower than 2000 kg ha<sup>-1</sup>. When annual gypsum application rates exceed 1000 kg ha<sup>-1</sup>, effects of magnesium amendment rates should be examined. The potential for disposal of large amounts of phosphogypsum on citrus acreage is not promising.

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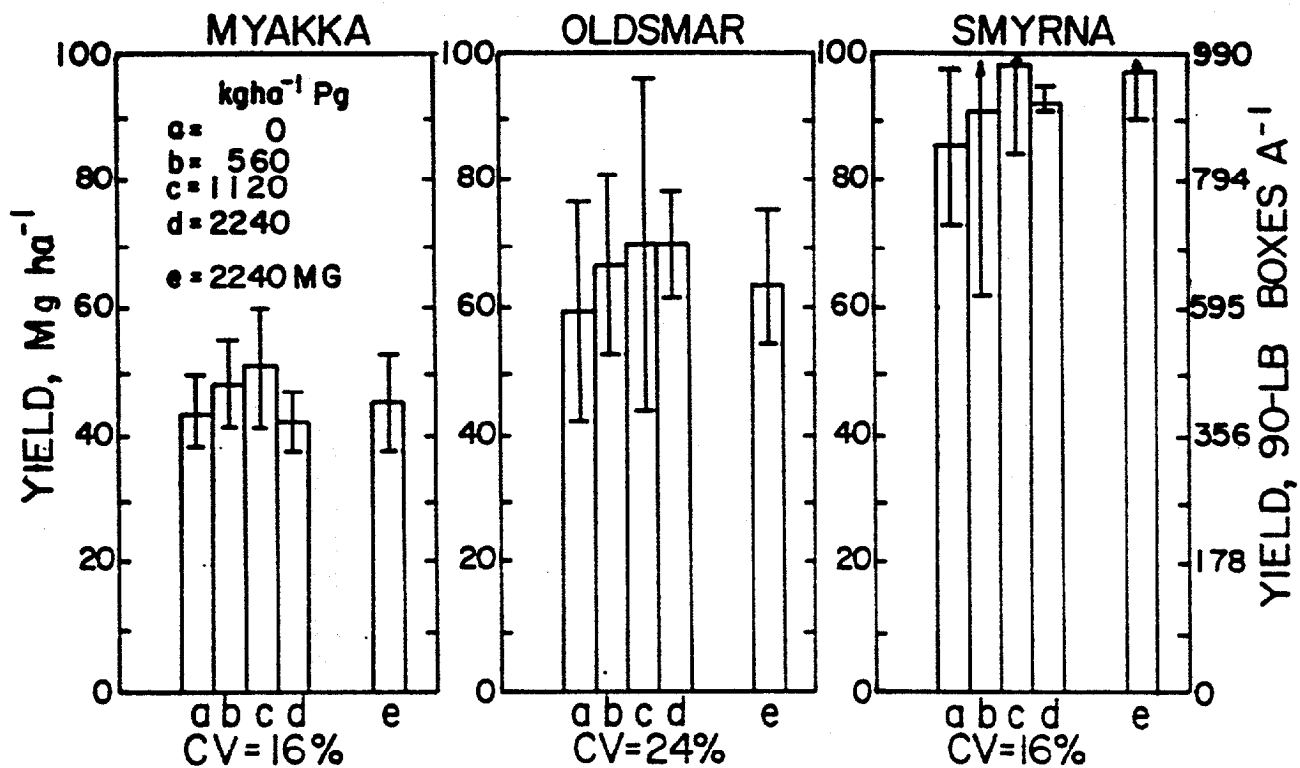


Fig. 1. Effects of phosphogypsum (Pg) rates and mined gypsum (MG) on yield of oranges harvested in 1988-89 on three soils. (Each yield bar is the mean of 4 values  $\pm$  SD).

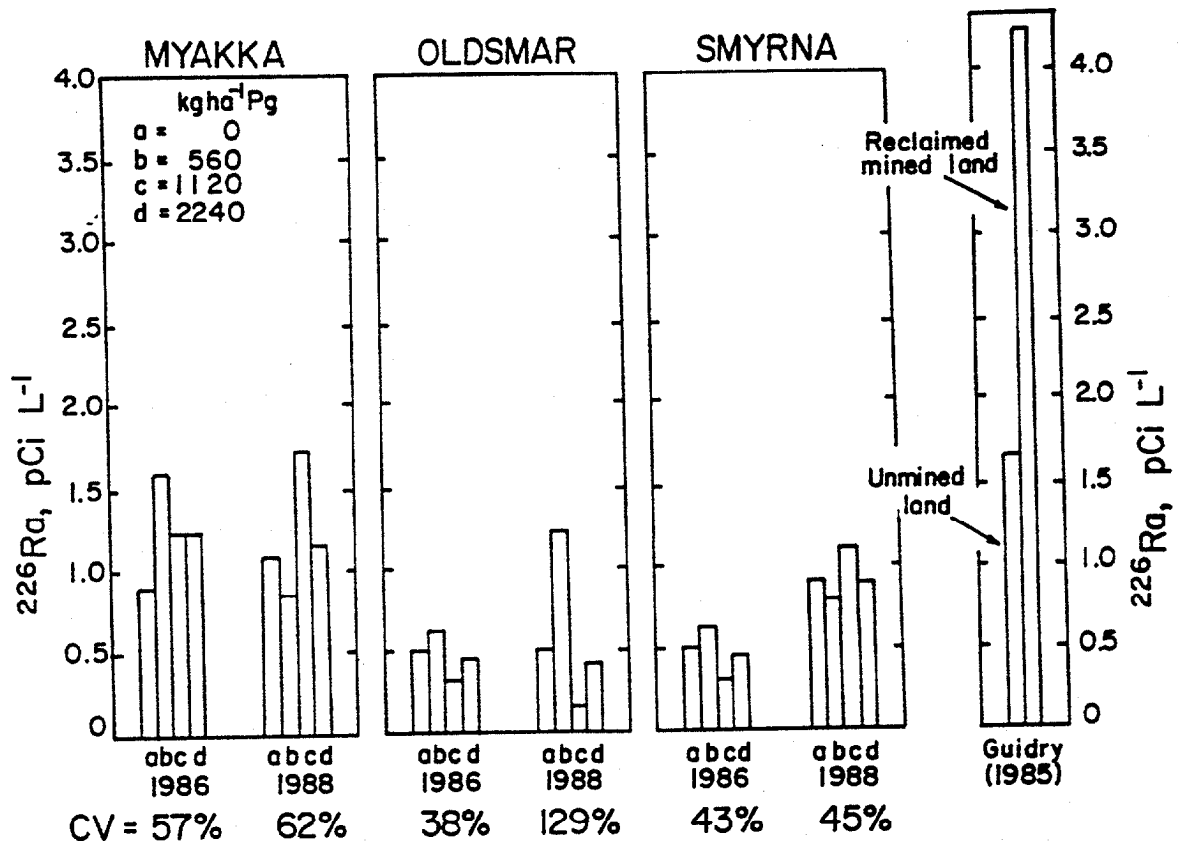


Fig. 2. Effects of phosphogypsum (Pg) rates on  $^{226}\text{Ra}$  concentration in oranges in comparison to Guidry's (1985) results on unmined land and reclaimed phosphate mined land.

Table 1. Effects of phosphogypsum (Pg) rate and mined gypsum (MG) on Brix of orange juice from trees grown on three soils.

Gypsum Rate (annual)	Soil Series		
	Myakka	Oldsmar	Smyrna
kg ha <sup>-1</sup>	----- Brix, % -----		
0 Pg	13.4	13.0	12.3
560 Pg	13.4	12.7	12.3
1120 Pg	13.6	12.7	12.2
2240 Pg	14.0	12.7	12.2
Mean, Pg	13.6	12.8	12.2
2240 MG	13.3	12.7	12.2
Mean, all	13.5	12.8	12.2
C.V., all (%)	3	3	4
	----- Pr > F -----		
Pg Rate	L*	NS	NS
Pg vs. MG at 2240 kg ha <sup>-1</sup> *		NS	NS

Nonsignificant (NS) or significant at the 0.05 (\*) probability level.

Table 2. Effects of phosphogypsum (Pg) rate and mined gypsum (MG) on titratable acidity of orange juice from trees grown on three soils.

Gypsum Rate (annual)	Soil Series		
	Myakka	Oldsmar	Smyrna
kg ha <sup>-1</sup>	----- Titratable Acidity, % -----		
0 Pg	0.92	0.98	0.67
560 Pg	0.90	0.93	0.65
1120 Pg	0.89	0.90	0.70
2240 Pg	0.84	0.90	0.67
Mean, Pg	0.89	0.93	0.67
2240 MG	0.87	0.90	0.68
Mean, all	0.88	0.92	0.67
C.V., all (%)	7.9	6.4	4.2
	----- Pr > F -----		
Pg Rate	NS	L*	NS
Pg vs. MG at 2240 kg ha <sup>-1</sup>	NS	NS	NS

Nonsignificant (NS) or significant at the 0.05 (\*) probability level.



Table 3. Effects of phosphogypsum (Pg) rate and mined gypsum (MG) on Brix/acid ratio of orange juice from trees grown on three soils.

Gypsum Rate (annual)	Soil Series		
	Myakka	Oldsmar	Smyrna
kg ha <sup>-1</sup>	----- Brix/Acid Ratio -----		
0 Pg	14.6	13.2	18.4
560 Pg	14.9	13.7	18.9
1120 Pg	15.4	14.2	17.8
2240 Pg	16.6	14.2	18.2
Mean, Pg	15.4	13.8	18.3
2240 MG	15.4	14.2	18.0
Mean, all	15.4	14.0	18.3
C.V., all (%)	8	6	9
	----- Pr > F -----		
Pg Rate	L*	L*	NS
Pg vs. MG at 2240 kg ha <sup>-1</sup>	NS	NS	NS

Nonsignificant (NS) or significant at the 0.05 (\*) probability level.

Table 4. Effects of phosphogypsum (Pg) rate and mined gypsum (MG) on mineral concentrations of 'Pineapple' orange juice from trees grown on Myakka soil.

Gypsum Rate (annual) kg ha <sup>-1</sup>	Juice Mineral Concentrations					
	Ca	K	Mg	P	Mn	Zn
	----- mg kg <sup>-1</sup> -----					
0 Pg	112	1563	122	182	0.44	0.44
560 Pg	116	1518	124	180	0.40	0.48
1120 Pg	122	1682	124	180	0.44	0.78
2240 Pg	130	1624	124	184	0.52	0.48
Mean, Pg	120	1597	124	182	0.45	0.54
2240 MG	122	1570	116	184	0.50	0.48
Mean, all	120	1591	122	182	0.46	0.53
C.V., all (%)	11	11	5	4	14	15
	----- Pr > F -----					
Pg Rate	L*	NS	NS	NS	x	NS
Pg vs MG 2240 kg ha <sup>-1</sup>	NS	NS	NS	NS	NS	NS

Nonsignificant (NS) or significant at the 0.10 (x) or 0.05 (\*) probability levels, respectively.

Table 5. Effects of phosphogypsum (Pg) rate and mined gypsum (MG) on leaf mineral concentrations of orange trees grown on Myakka soil.

Gypsum Rate (annual)	Leaf Mineral Concentration			
	Ca	K	Mg	P
kg ha <sup>-1</sup>	----- g kg <sup>-1</sup> -----			
0 Pg	34.8	20.7	4.0	1.65
560 Pg	36.0	20.7	3.9	1.53
1120 Pg	37.6	19.3	4.0	1.50
2240 Pg	35.8	20.4	3.3	1.53
Mean, Pg	36.0	20.3	3.8	1.55
2240 MG	41.8	20.1	3.7	1.52
Mean, all	37.2	20.2	3.8	1.54
C.V., all (%)	11	7	11	5
	----- Pr > F -----			
Pg Rate	NS	NS	L*Q*	L*Q*
1120 vs. 2240	NS	NS	**	NS

Nonsignificant (NS) or significant at the 0.05 (\*) or 0.01 (\*\*) probability levels, respectively.

Table 6. Effects of phosphogypsum (Pg) rate and mined gypsum (MG) on leaf mineral concentrations of orange trees grown on Oldsmar soil.

Gypsum Rate (annual) kg ha <sup>-1</sup>	Leaf Mineral Concentration			
	Ca	K	Mg	P
0 Pg	31.1	17.7	4.4	1.29
560 Pg	35.5	16.2	4.0	1.29
1120 Pg	34.5	15.7	4.0	1.34
2240 Pg	35.9	16.1	3.7	1.35
Mean, Pg	34.3	16.4	4.0	1.32
2240 MG	33.9	16.7	3.7	1.33
Mean, all	34.2	16.5	4.0	1.32
C.V., all (%)	9	12	10	5
	----- Pr > F -----			
Pg Rate	L*	NS	L*	L*

Nonsignificant (NS) or significant at the 0.05 (\*) probability level.

Table 7. Effects of phosphogypsum (Pg) rate and mined gypsum (MG) on leaf mineral concentrations of orange trees grown on Smyrna soil.

Gypsum Rate (annual)	Leaf Mineral Concentration			
	Ca	K	Mg	P
kg ha <sup>-1</sup>	----- g kg <sup>-1</sup> -----			
0 Pg	34.2	13.9	4.2	1.5
560 Pg	38.4	12.4	4.3	1.5
1120 Pg	35.3	13.3	4.2	1.4
2240 Pg	39.2	12.1	3.7	1.5
Mean, Pg	36.8	12.9	4.1	1.5
2240 MG	37.9	13.6	3.8	1.4
Mean, all	37.0	13.1	4.1	1.5
C.V., all (%)	9	12	8	3
	----- Pr > F -----			
Pg Rate	L*	NS	L*Q*	NS
Pg vs. MG at 2240 kg ha <sup>-1</sup>	NS	x	NS	NS

Nonsignificant (NS) or significant at the 0.10 (x) or 0.05 (\*), probability levels, respectively.

**The Trial Production Results from  
Demonstration Plant for Production of Ammonium  
Sulfate from Phosphogypsum**

by

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of Chemical Industry

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## Contents

1. Introduction
  2. Technical Basis
  3. Brief Introduction. to Technological Process
  4. Description of Trial-Production
  5. Conclusion
- References

# The Trial Production Results from Demonstration Plant for Production of Ammonium Sulfate from Phosphogypsum

## 1. Introduction

China, with a very large population, requires developed agriculture, and in order to develop agriculture, an adequate supply of chemical fertilizers is of the first importance. For this reason, the People's Republic of China has continually devoted major efforts to developing the chemical fertilizer industry since its founding. In 1989, the total output of chemical fertilizers in China reached 17.935 million tons (metric tons, the same here in after) of nutrients, second to the USSR and the USA, ranking third in the world. However, as the chemical fertilizer products in China, there still exists the problem of the  $N:P_2O_5:K_2O$  ratio in serious imbalance. Taking 1989 as an example, the output of nitrogenous fertilizers was 14.239 million tons of N (half of which came from medium -- and small scale plants with capacities of 10,000 to 100,000 tons of ammonia a year), that of phosphatic fertilizers was 3.663 million tons of  $P_2O_5$ , and that of potassic fertilizers 33,000 tons of  $K_2O$ . The output ratio of  $N:P_2O_5:K_2O$  was 1:0.257:0.0023, while the consumption ratio was 1:0.28:0.069. Consequently, China is energetically developing the production of phosphatic and potassic fertilizers, and it is expected that the output of phosphatic fertilizers will be doubled, by the year 2000. Newly built plants will, in the main, produce ammonium phosphates and compound fertilizers based on ammonium phosphates.

The intermediate, Wet-process phosphoric acid, in the production of ammonium phosphates will mostly be based on indigenous phosphate rocks.



The phosphate rocks in China are generally phosphorites, containing 31-34%  $P_2O_5$ , 46-48%  $CaO$ , 0.4-1.8%  $MgO$ , 3-3.5%  $R_2O_3$ , 2.5-3.5%  $F$  and 6-12% of acid-insoluble. When these rocks are used for the production of wet-process phosphoric acid by the dihydrate process, 4.5-5.0 tons of phosphogypsum are formed for a ton of  $P_2O_5$  in the form of acid. In planning the construction of numerous plants for the production of phosphatic and compound fertilizers, grave concern was shown over the disposal and utilization of large quantities of phosphogypsum.

In the early sixties, some scientific research institutions and phosphatic fertilizer plants in China carried out studies on the utilization of phosphogypsum, mainly on its use: (i) in the manufacture cement and sulfuric acid; (ii) in the production of ammonium sulfate; (iii) in the manufacture of gypsum boards and plaster; (iv) as cement retarder; and (v) as soil amendment.

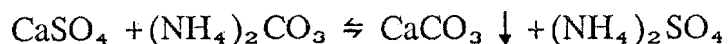
China has built two plants to produce cement and sulfuric acid based on phosphogypsum, their annual capacities being 40,000 and 100,000 tons of sulfuric acid, respectively,. With regard to the technology for the production of ammonium sulfate from phosphogypsum, it has been mastered through laboratory study in the sixties, but due to the rapid expansion of urea production, it is difficult for ammonium sulfate based on gypsum to compete with urea. Since the mid-eighties, the construction, of medium and small-scale ammonium phosphate plants has progressed in China, and with a view to solving the problem of phosphogypsum disposal and balance in nitrogenous and phosphatic fertilizer production, a new process has been developed for the integration of ammonium phosphate production with the traditional ammonium bicarbonate production (a unique process for the production of nitrogenous fertilizer in China) for the production

of ammonium phosphate-sulfate.

In 1986, Shanghai Research Institute of Chemical Industry and No.3 Design Institute; both under the Ministry of Chemical Industry, cooperated to set up a productive experimental workshop for wet-process phosphoric acid, ammonium phosphate and ammonium sulfate based on phosphogypsum (80 tons of ammonium sulfate a day) as an accessory to the unit of 10,000 tons of ammonia a year at Maanshan Municipal Chemical Fertilizer Plant in Anhui Province. This paper presents primarily the technical features of the section of ammonium sulfate production based on phosphogypsum in the plant and the operation results during trial-production.

## 2. Technical Basis

The chemical basis for the, production of ammonium sulfate from gypsum is the chemical reaction discovered by Merseburg:



On account of the very low solubility of  $\text{CaCO}_3$ , at  $25^\circ \text{C}$  with a concentration of ammonium carbonate solution of 0.125 N, the equilibrium constant of the reaction  $K=4820$ , and the equilibrium conversion of calcium sulfate can reach 99.97%.

From the point, of the reaction kinetics, the main factors that exert an influence on the reaction rate are the surface area of calcium sulfate and the diffusion rate of the reactants and products. The particles of phosphogypsum are rather fine, with an average particle size of <30 microns, thus providing an adequate reaction surface. When the reaction product, ammonium sulfate, is already present in the liquor, the solubility of calcium sulfate increases, so the dissolution rate of gypsum also increases, facilitating the conversion process. If suitable stirring intensity maintains

in the conversion reactor, the conversion of the phosphogypsum can attain a satisfactory level within 1 hour, as shown by the experiments conducted in the stirred-tank reactor.

When the chemistry involved is clear, another factor that determines the production efficiency is the crystallization of calcium carbonate formed in the reaction, which is a complex process involving the simultaneous occurrence of chemical reaction with formation of crystals. Through detailed study, it has been found that the most important factor is to control the concentration of excessive  $\text{CO}_3^{=}$  in the reaction-crystallization slurry, so as to form aggregated crystal clusters, which exhibit excellent filtration properties.

In respect of the very low solubility product of  $\text{CaCO}_3$ , excessive agitation is an important factor inducing the formation of crystal nuclei, but stirring with too low an intensity goes against the high diffusion rate required for the dissolution of gypsum. Therefore, the appropriate intensity of agitation should be given depends on the type of conversion equipment used.

Phosphogypsum contains various inorganic impurities and a little organic matter. Some organic substances come from the phosphate rock, while other from the flotation agent for beneficiation and the anti-foaming agent added in the production of phosphoric acid. The organic matter decomposes into tarry colloids under the pH value and temperature used in phosphoric acid production, thus increasing the viscosity of the solution and resistance to diffusion.

The free phosphoric acid that has not been completely washed out remains in the phosphogypsum will react with ammonium carbonate to form diammonium phosphate, which then reacts with calcium sulfate,

forming dicalcium phosphate and tricalcium phosphate. These calcium phosphates produced under alkaline conditions are in the form of fine particles.

The majority of the impurities present in phosphogypsum affects the growth of calcium carbonate crystals, which become rather fine; leading to poor filtration and washing indices for calcium carbonate in the conversion slurry. In order to reduce the effect of impurities, phosphogypsum should undergo proper treatment before going into the conversion system.

From the afore-said basic essential concerned, it is evident that various technical measures are to be taken to overcome unfavorable factors in the production of ammonium sulfate from phosphogypsum and an engineering design geared to practical needs is to be thought out for the realization of smooth operation in commercial production.

### **3. Brief Introduction to Technological Process**

The process used in the commercial experimental workshop is shown in Fig.1, including sections for the purification of phosphogypsum, preparation of ammonium sulfate-carbonate solution, conversion reaction and filtration of converted slurry, neutralization and decarbonation of ammonium sulfate filtrate and its evaporation and crystallization, and separation and drying of ammonium sulfate crystals, which will be explained in succession below.

#### **Purification of phosphogypsum**

The phosphogypsum cake discharged from the tilting-pan filter in the wet-process phosphoric acid workshop is slurried with the addition of water in a slurring tank, from which the gypsum slurry flows to a rinsing tank, to rinse out most of the colloidal organic matter and fine particles.

The underflow from the rinsing tank enters a baffling tank, where the concentration of the gypsum slurry is adjusted to the specified value by means of an automatic density controller. The required amount of gypsum slurry is then pumped to a belt filter for filtration and washing, to remove most of the free acid and colloids in the phosphogypsum, accomplishing the purpose of purification.

The automatic control system for the density and flow rate of the gypsum slurry is technically the key in the process, which solves the problem of accurate metering and control of phosphogypsum feed into the conversion tank, to ensure the proper carrying out of the conversion reaction.

#### **Preparation of ammonium sulfate-carbonate solution**

The special feature of this process technology is to utilize the decarbonation sector in the small-scale nitrogenous fertilizer plant producing ammonium bicarbonate for the preparation of ammonium carbonate solution, that is to say, to use directly the converted gas with a high carbon dioxide content from the shift reaction of semi-water gas with steam to carbonate aqua ammonia for the preparation of ammonium carbonate solution. Also the wash liquor containing some ammonium sulfate from the filtration and washing of converted slurry is used to prepare aqua ammonia instead of using clean water, thereby reducing the amount of water introduced into the system, so as to prepare ammonium sulfate-carbonate solution with the highest possible concentration, favoring the conversion reaction of phosphogypsum in the next section.

The carbonation tower operates under a pressure of 0.6- 0.7MPa. The gas leaving the top of the tower contains <0.2% of carbon dioxide,

and the tail gas after passing through another 'scrubber. to ensure safety enters a compressor and then goes to the cuprous ammonia liquor scrubbing section of the ammonia unit.

### **Conversion System**

The conversion system consists of conversion reactors and a filter. There are altogether three conversion reactors in series, being stirred tanks of the same volume equipped with agitators of the propeller type, the speed of which can be adjusted.

The filtration of the converted slurry is conducted on a rubber belt vacuum filter, which can be arranged for two or three counter-washings, to thoroughly wash calcium carbonate and suck out water to a fairly low moisture content, thus facilitating dry disposal. The filtrate containing 36-38% of ammonium sulfate is sent to the evaporation and crystallization system.

#### **Evaporation and crystallization of ammonium sulfate solution**

The ammonium sulfate filtrate contains some ammonium carbonate, which is neutralized with sulfuric acid for transformation into ammonium sulfate, expelling carbon dioxide, before it is fed into the evaporator-crystallizer.

The evaporator-crystallizer is externally heated and of the forced circulation type, which favors the increase in heat transfer coefficient of the heater and plays an important role in the control of nucleus formation in the supersaturated ammonium sulfate supersaturation in the crystal growth zone.

A double-effect evaporator-crystallizer is used, to lower steam

consumption in the evaporation and crystallization of ammonium sulfate solution.

### Separation and drying of ammonium sulfate crystals

The ammonium sulfate crystal magma is separated by a push-type continuous centrifuge, the ammonium sulfate crystals pushed out are sent to a pneumatic dryer for drying, and ammonium sulfate products is obtained.

#### 4. Description of Trial-Production

During trial-production feed was introduced at 70% of the design capacity. The feeding rate for the conversion reactor was 3.80 tons of phosphogypsum, per hour (dry basis) and 5.24 tons of ammonium carbonate solution per hour.

The phosphogypsum after washing had the following composition (dry basis):

Constituent	CaO	SO <sub>3</sub>	H <sub>2</sub> O-soluble P <sub>2</sub> O <sub>5</sub>	Insoluble P <sub>2</sub> O <sub>5</sub>	acid insoluble	Water of crystallization
Content, Wt%	30.30	43.10	0.10	0.49	4.68	19.30

This showed that ideal results were obtained from the purification by rinsing of phosphogypsum, the purity of which was 92.70%. CaSO<sub>4</sub> • 2H<sub>2</sub>O.

Ammonium carbonate solution was prepared mainly under the control of automatic control meters and instruments. The ammonium carbonate solution prepared had yet to be sampled manually and analyzed for its concentration and ratio of 2NH<sub>3</sub>/CO<sub>2</sub> in the solution. The CO<sub>2</sub> content of the gas effluent from the absorber was continuously indicated by means of an infrared automatic analyzer, so the operators needs only to adjust

properly the rate of converted gas and aqua ammonia fed into the absorber according to the CO<sub>2</sub> content.

The feeding rate of the conversion reactor was automatically controlled in line with the value fixed in the control room and adjusted according to sampling and analytical results of the slurry liquid phase in the conversion tank. The liquid phase of the slurry in the No.1 conversion reactor was usually controlled to give 20-25g of ammonium carbonate per liter. The temperature of the slurry was, raised with the aid of a steam jacket and maintained at 65-70°C. The intensity of agitation was controlled that the solids in the slurry would not precipitate. These were the optimum conditions for the conversion of gypsum and the crystallization of calcium carbonate.

The microphotographs taken by the SEM of the calcium carbonate crystals precipitated in trial-production are shown in Fig.2. The particle size of the spherical aggregates was in the range of 30- 80 microns. These crystals were easily filterable. The belt filter ran steadily, and the operation was quite ideal.

The analytical results of the calcium carbonate cake showed that the conversion of phosphogypsum was 96-98%, and the washing rate of ammonium sulfate from the filter cake was > 98%.

The trial-production proved that, there was a great production potential for the conversion reactor and filter chosen.

The discharge from the ammonium sulfate evaporator- crystallizer contained 20-25%(wt.) of ammonium sulfate crystals, which, after separation from the centrifuge, had a N content of 20.80%, free sulfuric acid 0.05%, and moisture 1.8% and when dried to a moisture of <0.5%, had a N content of 21.00%.



As the pH value of the ammonium sulfate solution was not controlled in a very steady manner before its evaporation and crystallization, the ammonium sulfate crystals formed were thin and long rhombic ones, ~2mm in length and 0.5mm in width and thickness, which broke during drying, and it was planned to readjust the pH value and other condition in crystallization.

Based on the main indices reached in the trial-production, an estimation was made on the consumption of raw materials and utilities per ton of ammonium sulfate under full-load production:

Item	Unit consumption
<b>Raw materials:</b>	
Ammonia, 99.5% NH <sub>3</sub>	0.272 ton
Sulfuric acid, 93% H <sub>2</sub> SO <sub>4</sub>	0.064 ton
phosphogypsum, 92.5% CaSO <sub>4</sub> ·2H <sub>2</sub> O	1.53 ton
CO <sub>2</sub>	0.37 ton
<b>Utilities:</b>	
Water, circulating	200 m <sup>3</sup>
process	4.5 m <sup>3</sup>
Electricity, 380V, 3-phase	70 kwh
Steam, 0.8 MPa	0.2 ton
0.35 MPa	1.2 ton
Instrument air, 0.6 MPa	20 m <sup>3</sup>

From the above consumption figures, workshop overhead and various other expenses, a calculation was made on the ex-plant sale cost, of which raw material cost took 57.21%, utilities 14.52% , and others 28.27%. The proportion of utilities and other costs was rather high in the cost, while

that of raw materials low, reflecting the special features of the production of ammonium sulfate from phosphogypsum.

## 5. Conclusion

Under the circumstances of devoting major efforts to developing high-analysis compound fertilizers in China, the disposal and utilization of phosphogypsum are urgent issues to be settled. China is poor in sulfur resources, so that the technical route of manufacturing ammonium sulfate from phosphogypsum is of special significance. With this technique, some of the existing medium-and-small-scale ammonium bicarbonate plants can be retrofitted to produce ammonium sulfate or ammonium sulfate-phosphate, which not only increases the output of phosphatic fertilizers but also improves the quality of the nitrogenous fertilizer.

The conclusions drawn from the commercial tests on the production of ammonium sulfate from phosphogypsum are as follows:

- i. The technological process is rather long for the production of ammonium sulfate from phosphogypsum and covers many chemical unit operations. Its primary link is the conversion reaction, the key technology of which is the control of crystallization conditions for the formation of calcium carbonate crystals.

One of the effects on conversion and crystallization is that of the various impurity components of phosphogypsum, consequently, it is necessary to put up a simple and efficient operation for the purification of phosphogypsum, to remove most of the organics, colloidal particles and free phosphoric acid.

Other factors favorable to the good filtration of calcium carbonate crystals are mainly: the control of ammonium carbonate content in the

conversion reaction slurry to give an appropriate excess; the control of agitation intensity to keep the solids in the reaction slurry in uniform suspension; and the residence time of the reaction slurry in the No.1 reactor not over 1 hour.

ii. Excellent results have been obtained from some technical measures taken in the commercial tests: (a) the direct carbonation of aqua ammonia with converted gas to produce ammonium sulfate-carbonate solution; (b) the automatic control of the density and flow rate of the phosphogypsum suspension, in combination with the selection of a belt filter to filter and wash the phosphogypsum suspension, ensuring the purity of phosphogypsum and the accuracy in metering the feed.

The above measure (a) brings about a closer relation of the ammonia unit with the ammonium sulfate from gypsum workshop, and practical work proves that the decarbonation of converted gas proceeds quite satisfactorily, which may fully replace the conventional process for the preparation of ammonium carbonate solution with  $\text{CO}_2$  desorbed from other decarbonation routes.

iii. Techno-economic problem in the production of ammonium sulfate from phosphogypsum lies mainly in the low nitrogen content of ammonium sulfate, its production cost based on unit nitrogen being considerable higher than that of urea and ammonium nitrate. Nevertheless, the ammonium sulfate-phosphate or ammonium sulfate product from this process improves the nitrogen utilization after its application, and partly solves the problem of phosphogypsum disposal in the development of the phosphatic fertilizer industry, which is of great practical significance in China to revamp some ammonium bicarbonate plants with favorable conditions combining the production of nitrogenous and phosphatic fertilizers by the adoption of this technical option.

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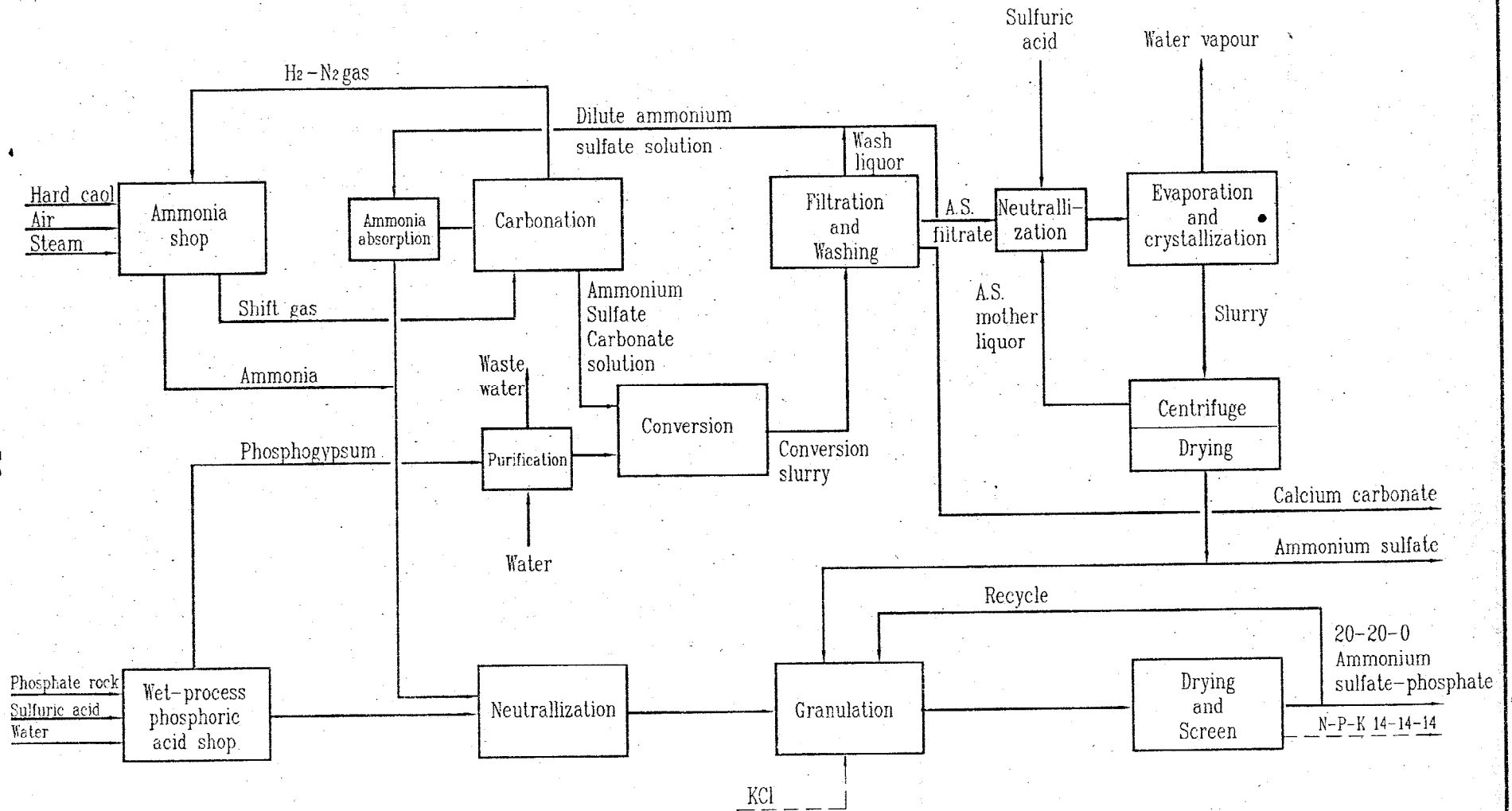
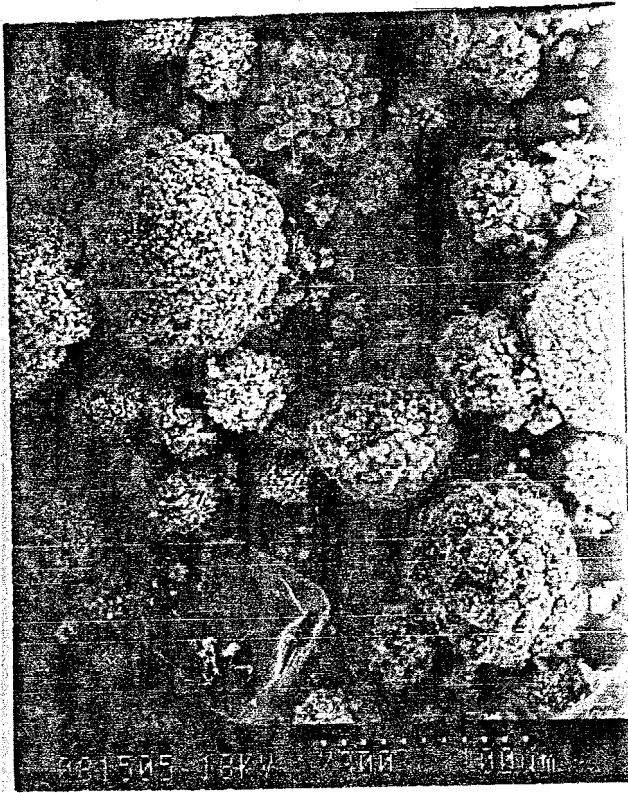
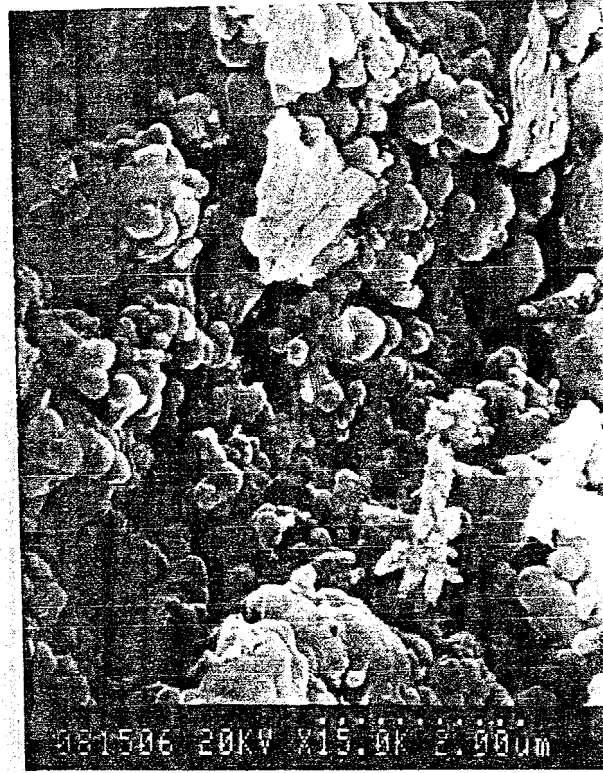


Fig1. Flowsheet for production of ammonium sulfate from phosphogypsum



X300

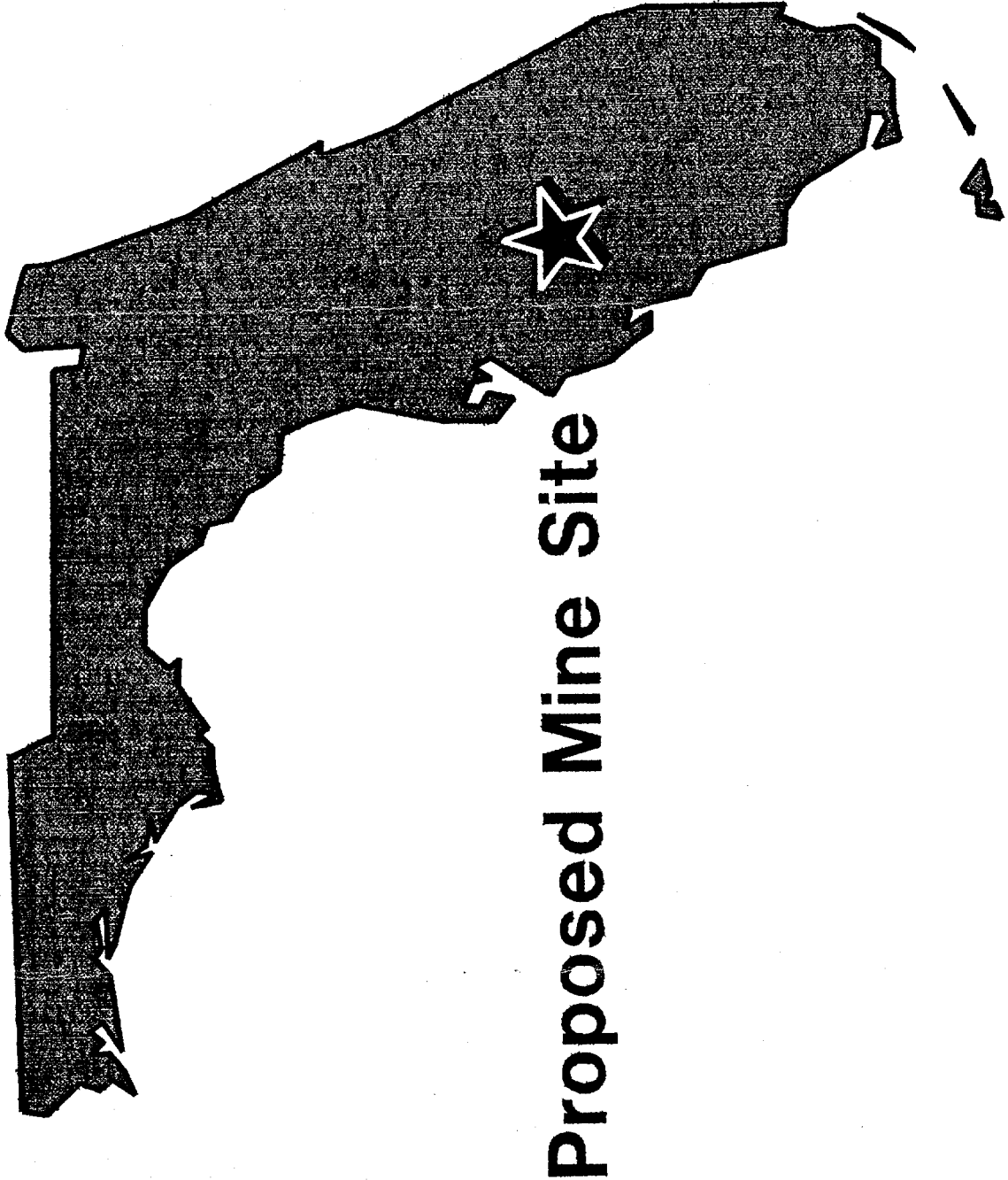


X15,000

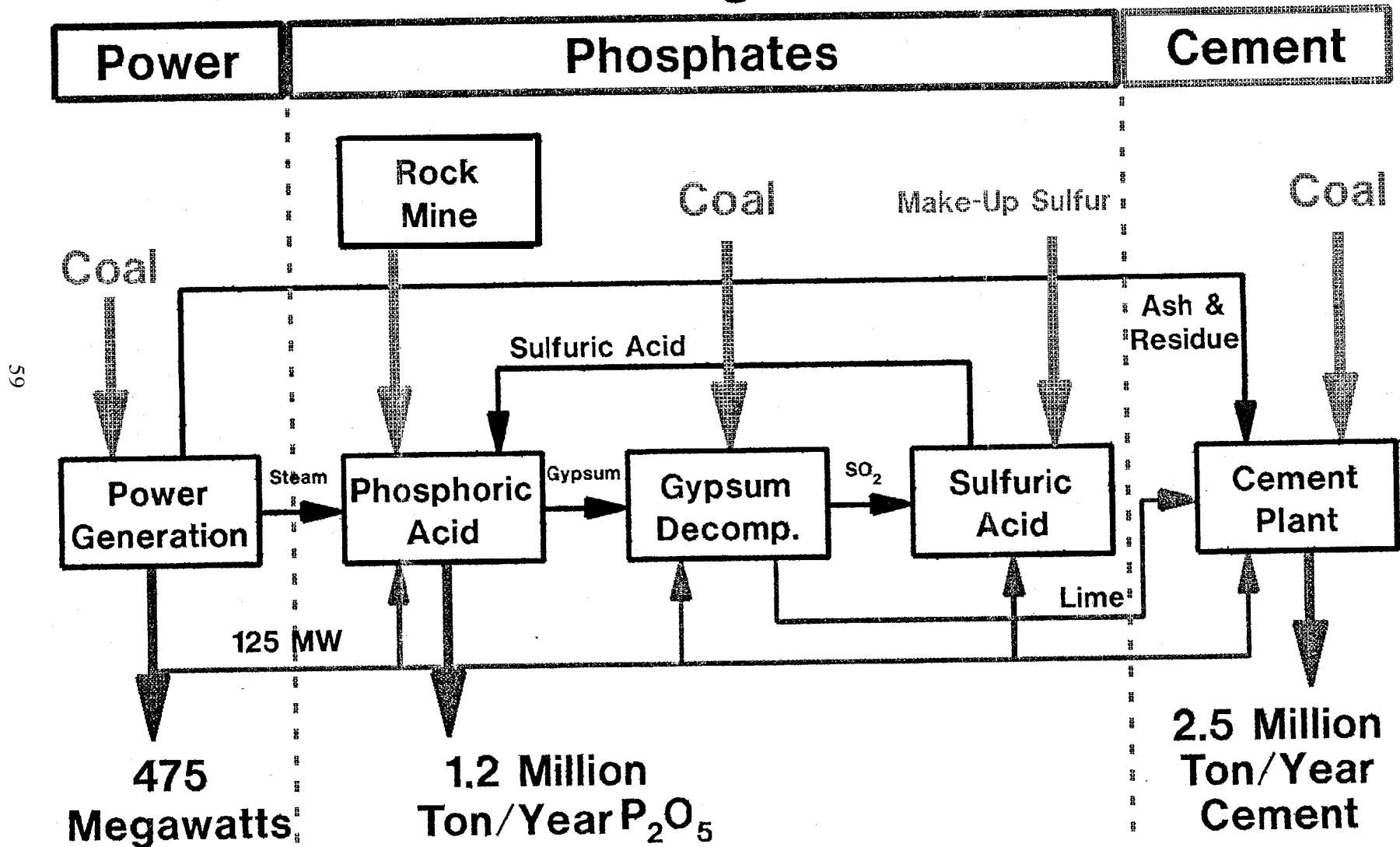
Fig2. The SEM photograph of calcium carbonate obtained in the trial production

INTEGRATION AND ECOPHOS ARE KEY TO THE PINE LEVEL PROJECT

Supplement



# CMI Pine Level Cogeneration Project

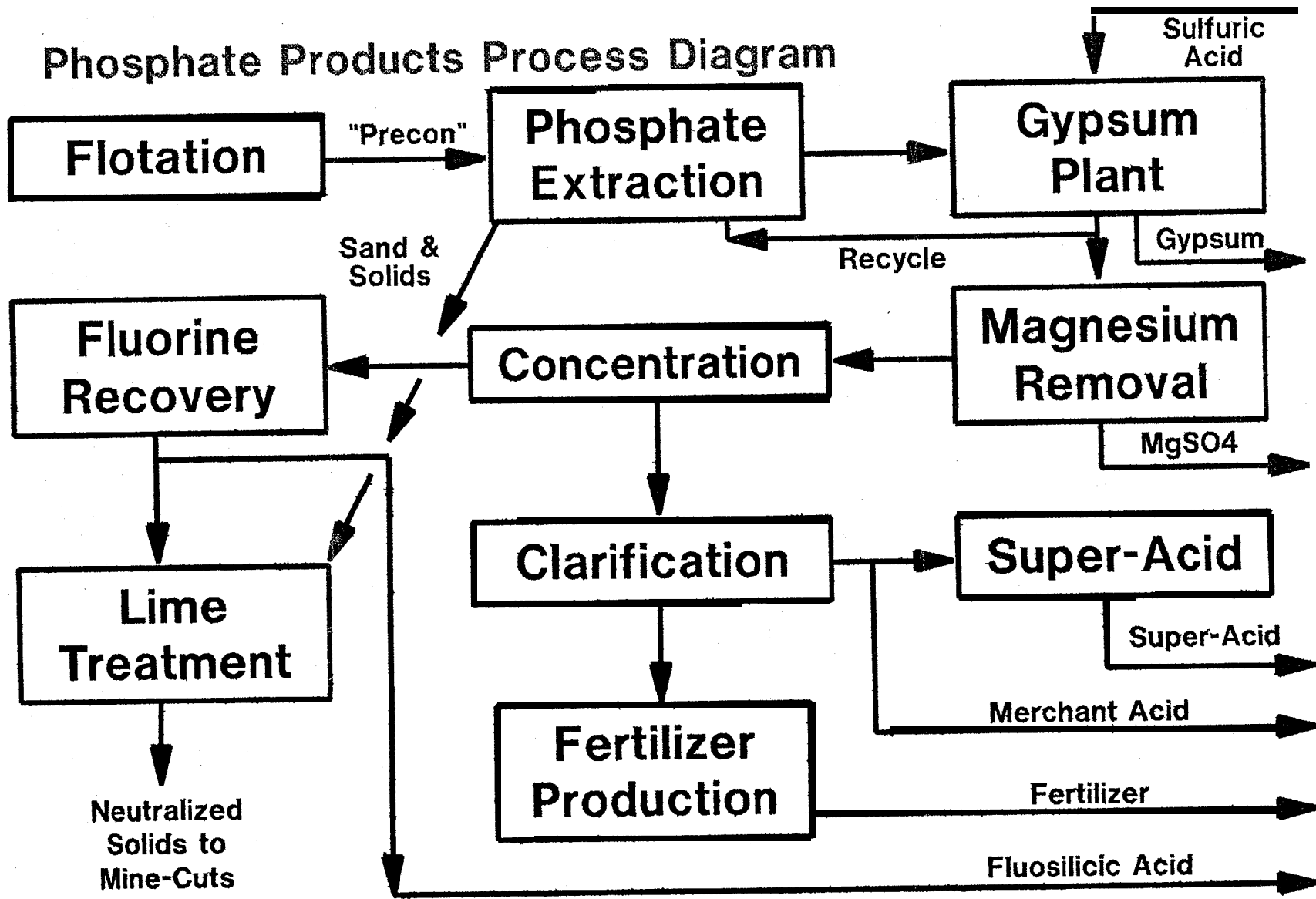




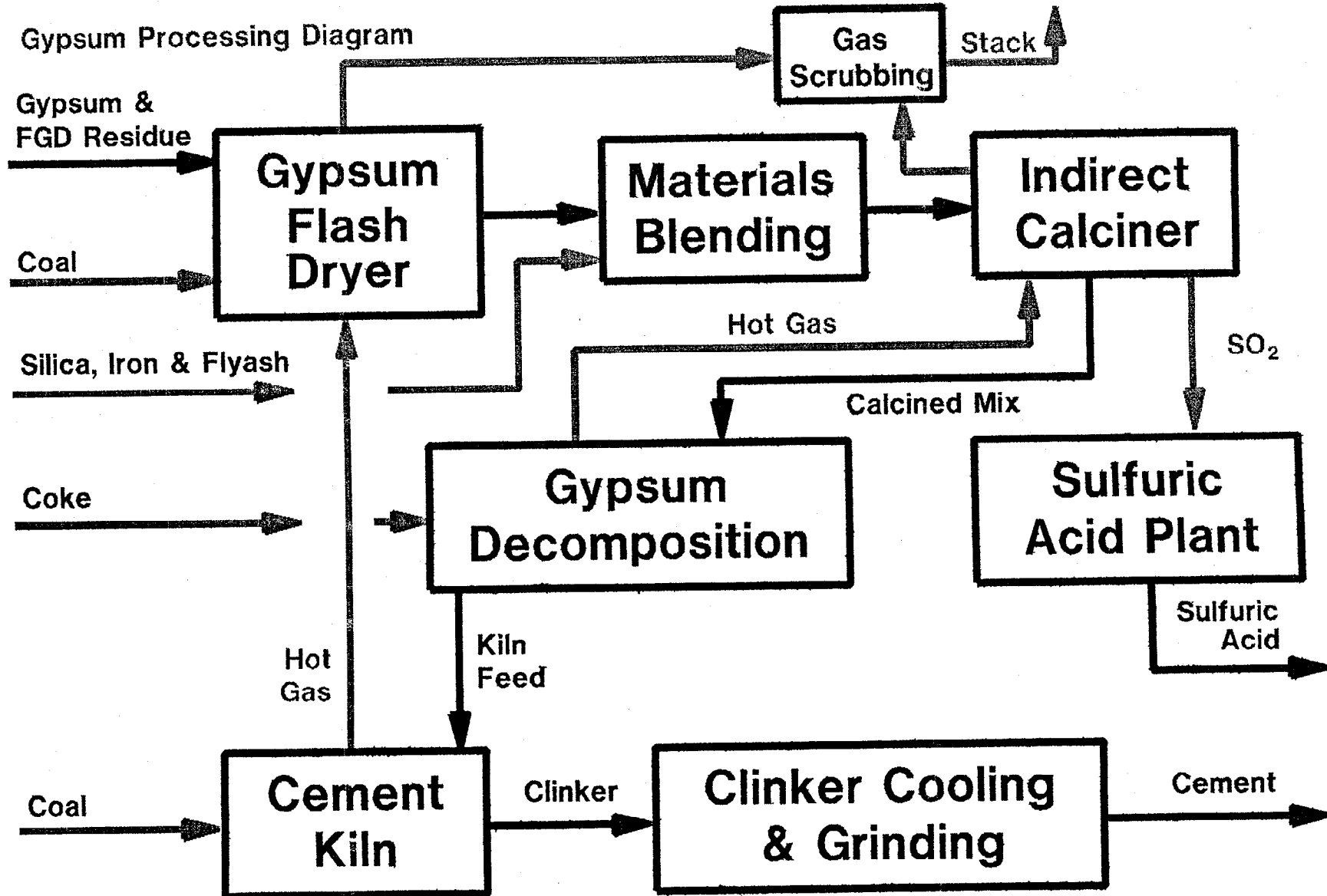
## Pine Level Capacities

<b>Power Plant</b>	<b>660 MW, coal fired</b>
<b>Mine</b>	<b>20 million ton per year of matrix</b>
<b>Phosphate Products</b>	<b>5 million ton per year of pre-concentrate</b>
	<b>1.1 million ton P<sub>2</sub>O<sub>5</sub> per year of fertilizer products</b>
<b>Cement</b>	<b>2.6 million ton per year of Portland cement</b>
<b>Sulfur recycle</b>	<b>1 million ton per year of sulfur equivalent recycled</b>

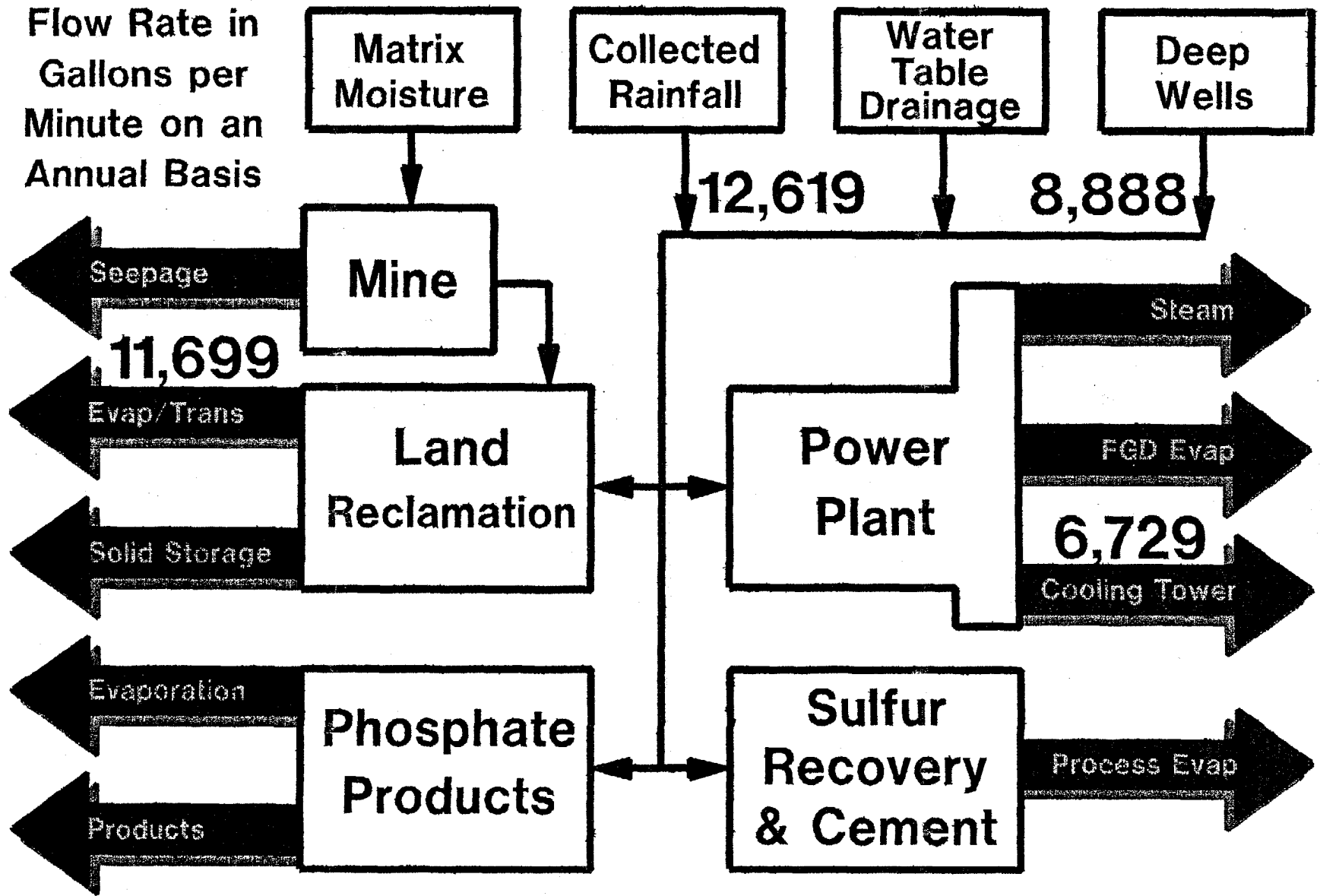
# Phosphate Products Process Diagram



Gypsum Processing Diagram



Flow Rate in Gallons per Minute on an Annual Basis



63

## **PANEL DISCUSSION: THE FUTURE OF PHOSPHOGYPSUM**

**Contribution by J. Beretka**

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The members of the Panel were requested by the Chairman, Mr G. Michael Lloyd, Jr, to address the following two questions: Firstly, what do members of the Panel think they should do about the utilisation of phosphogypsum, and secondly, how to go about it? Due to the fact that my expertise has been in the area of building materials, particularly plaster of Paris ('stucco'), plasterboard and cement, I would like to restrict my contribution to the above materials. Furthermore, I would like to restrict my comments to the Australian situation.

### **INTRODUCTION**

The technology for the utilisation of phosphogypsum in many areas has already been solved. These include its application as a soil conditioner in agriculture, production of cement and sulfur, road construction and road aggregates, its application as a retarder in Portland cement, and also for making plaster products such as plaster of Paris and plasterboard. Its more widespread use in some countries is hampered by (a) the potential radioactivity of some of the materials generated by the different phosphoric acid processes employed; (b) the higher costs involved in purifying or handling the material; (c) the general apprehension of the potential users and general public in understanding the radiological effects of the impurities present in the material; (d) the effect of major impurities, particularly phosphate and fluoride, in the processes subsequently employed (e.g. 'lime sensitivity') (Beretka, 1988); and (e) most importantly, vested interest by suppliers of natural gypsum and producers of gypsum products.

Before turning to building materials, particularly to plaster products, the point should be emphasised that there are great differences between the impurity contents of phosphogypsum generated by the different phosphoric acid processes. In particular, phosphogypsum generated by single-stage crystallisation processes (e.g. Prayon) contains higher levels of impurities, including radioactive impurities, than those materials generated by two-stage crystallisation processes (e.g. Nissan, Fisons, NKK). From the technological point of view, it is usually easier to process the materials generated by two-stage processes than those derived from single-stage processes, due to their lower levels of impurities, in particular  $P_2O_5$  and  $F^-$  contents. Phosphate and fluoride appear to be the most important impurities from the point of view of phosphogypsum utilisation in the building and particularly the plaster industry.

### **BUILDING MATERIALS**

From the point of view of the application of phosphogypsum for making building materials, two important conditions have to be considered. Firstly, the material has to be available in large quantities, and secondly, the material has to be inexpensive. Phosphogypsum appears to fit the above two conditions perfectly.

In Australia, all the material generated is produced by either the Nissan or Fisons, two-stage crystallisation process. Industry practice in the past (Beretka, 1980; 1990), and more recent experiments carried out at CSIRO (Brown and Beretka, 1990), have shown that the material can successfully be converted to (a) plaster of Paris, plasterboard and plaster products; and (b) a new type of low energy binder/cement, termed Novel Cement (Valenti, *et al.*, 1988; Beretka, *et al.*, 1990). Most probably the material is also suitable as a retarder for Portland cement, but in Australia we have no experience in this particular area due to the fact that the country is very rich in natural resources, which includes natural gypsum. Consequently, at present only natural gypsum is used for such purposes.

## **CONVERSION OF PHOSPHOGYPSUM TO BUILDING MATERIALS**

Knowledge of the gamma-ray activity of the material to be used for building materials is important. There seems to be little relationship between the gamma-ray activity of a phosphogypsum stockpile ('stack') and the radon exhalation rate of the product material, so it is important to measure the total radiation dose from the product rather than the raw material. This may be illustrated by recent experiments (Brown and Beretka, 1990) carried out at CSIRO in making plasterboard from phosphogypsum. This particular material had gamma activity of approximately 10-12 pCi/g, mostly due to the presence of  $^{226}\text{Ra}$ . Measurements carried out at the Australian Radiation Laboratories (O'Brien, *et al.*, 1991) showed that the total annual effective dose equivalent (i.e. from exposure to gamma-radiation and radon gas) from this processed phosphogypsum plasterboard was approximately 600 micro-Sieverts, provided the ventilation rate was kept above 0.5 air changes per hour. This value is well below the ICRP (1987) recommended limit of 1 milli-Sievert per year for members of the public.

## **CONCLUSIONS**

Phosphogypsum is suitable for making plaster products and plasterboard for application in the building industry. Furthermore, by coating the phosphogypsum-plasterboard with cardboard (in order to simulate commercial plasterboard), or with wallpaper or paint, the radon emanation from the board can be reduced even further than the 600 micro-Sievert per annum measured in the uncoated material. It is imperative, however, that the radioactive trace element content, and the gamma-ray activity content of the bulk samples, is measured, together with the radon emanation from the product. It is important to get the latter measurements done by an independent organisation such as the Australian Radiation Laboratories, or any other similar body operating in other countries. Finally, it is most important to educate the general public about the safety of building materials containing very low levels of radioactivity, such as plaster products made from phosphogypsum.

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3rd International Conference on Phosphogypsum - December, 1990

"The Future of Phosphogypsum"

Panel Discussion - Robert Ho, Florida DOT

I am speaking as a highway engineer - a minority among this group of chemists here. Assuming that the environmental issues surrounding phosphogypsum have been resolved, there should be more laboratory and field research to study the use of phosphogypsum as a highway construction material. A preliminary laboratory investigation was performed by FDOT on several sources of phosphogypsum in the mid-eighties for possible use as an embankment material in highway construction.

The two experimental county roads in Polk and Columbia counties are a first step in the right direction in the field testing of phosphogypsum-soil mixtures as base for low volume roads. Florida DOT has an ongoing program to evaluate industrial, construction and other waste products for possible highway construction applications. A 3-stage testing program consisting of laboratory, test pit and field test sections has been developed by the Department for the evaluation of new materials as possible pavement base component.