

Publication No. 05-040-111

# BEHAVIOR OF RADIONUCLIDES DURING AMMONOCARBONATION OF PHOSPHOGYPSUM

*Prepared By*

Department of Oceanography  
Florida State University

*under a grant sponsored by*



March 1995

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

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

## **Research Staff**

### **Executive Director**

**Richard F. McFarlin**

### **Research Directors**

**G. Michael Lloyd Jr.  
Jinrong P. Zhang  
Steven G. Richardson  
Gordon D. Nifong**

**-Chemical Processing  
-Mining & Beneficiation  
-Reclamation  
-Environmental Services**

Florida Institute of Phosphate Research  
1855 West Main Street  
Bartow, Florida 33830  
(863) 534-7160  
Fax:(863) 534-7165

# **BEHAVIOR OF RADIONUCLIDES DURING AMMONOCARBONATION OF PHOSPHOGYPSUM**

FIPR Project #93-05-040R

## **FINAL REPORT**

William C. Burnett  
Michael Schultz  
Carter Hull

Environmental Radioactivity Measurement Facility  
Department of Oceanography  
Florida State University  
Tallahassee, Florida 32306  
Tel: 904-644-6703  
email: [burnett@ocean.fsu.edu](mailto:burnett@ocean.fsu.edu)

March 6, 1995

## **DISCLAIMER**

The contents of this report are reproduced herein as received from the contractor.

The opinions, findings and conclusions expressed herein are not necessarily those of the Florida Institute of Phosphate Research, nor does mention of company names or products constitute endorsement by the Florida Institute of Phosphate Research.

## PERSPECTIVE

Gordon D. Nifong, Ph. D.

Florida Institute of Phosphate Research

Some 30 million tons of phosphogypsum (hydrated calcium sulfate) are produced yearly by the Florida phosphate industry as a by-product of phosphoric acid manufacture. A very small amount is used in agriculture, but the vast majority, perhaps 99%, is simply conveyed by acidic water slurries to stacks for stockpiling at the plant site. Utilization of the material is prevented largely by the presence of radioactive impurities, mainly radium, polonium, and lead. A major research goal of the industry for two decades has been to find some use for the gypsum that would be practical, economical, and environmentally acceptable.

Elsewhere in the world, mainly in Asia, phosphogypsum is reacted with ammonium carbonate to produce ammonium sulfate and calcium carbonate, i. e. the "Merseberg" process. Ammonium sulfate has value as a fertilizer, and the calcium carbonate, or calcium oxide therefrom, might have value in helping neutralize acidic waters from phosphate industry operations. In the process phosphogypsum is consumed and two potentially useful materials are produced from one by-product. One factor in determining whether or not the process might have value to the Florida industry is the fate of the radionuclides in the gypsum. This current research confirms that most radionuclides follow the calcium carbonate, leaving a relatively "clean" ammonium sulfate.

At the present time the process does not seem economically viable. A relatively small amount of ammonium sulfate is used in the U. S. because of its low nitrogen content. Use may well increase in the future because of the need to return sulfur to the soil, but currently there is adequate ammonium sulfate from other, established, sources. Calcium carbonate could be useful in neutralizing the acidic process water from phosphoric acid manufacture, and the volume of carbonate produced would be smaller than the volume of gypsum consumed, but calcium carbonate is not very stackable, and hence production would have to follow demand rather rigorously.

This project has accomplished its purpose of determining the fate of radionuclides following the Merseberg reaction. Practical use of the information will come only if there is a marked change in economic or regulatory status.

## ABSTRACT

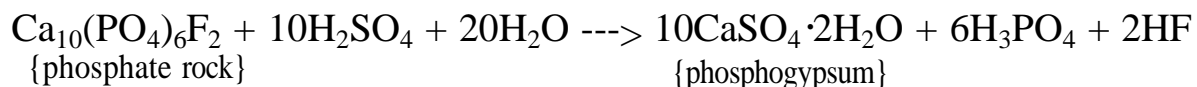
Approximately thirty million of tons of by-product “phosphogypsum” are currently produced annually by the phosphate fertilizer industry in Florida. Nearly all of this material is stockpiled because radioactive impurities prevent utilization of what could otherwise be a useful agricultural amendment or construction material. Long-term storage and maintenance of this material presents economic as well as potential environmental concerns. One partial solution to this problem may be conversion of phosphogypsum to ammonium sulfate by the so-called “Merseberg” ammonocarbonation process. Ammonium sulfate is an excellent fertilizer which supplies sulfur as well as nitrogen to soils.

We have assessed the flow of the natural decay-series radionuclides  $^{238}\text{U}$ ,  $^{226}\text{Ra}$ ,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  through the Merseberg process by analysis of starting materials and products from overseas industrial-scale plants. Results indicate that the radionuclides associated with phosphogypsum do not report to the ammonium sulfate product but are found instead almost exclusively in the by-product calcium carbonate. Thus, the radiochemical results are encouraging in terms of using this process as an option for partial removal of waste phosphogypsum. Although there is a clear and recognized need for increased sulfur addition to many crops, the price of sulfur has been so low and alternative supplies of ammonium sulfate so common that investment in this process has been discouraged. Recent price increases and enhanced demand for ammonium sulfate may make the Merseberg process more attractive in the future.

# INTRODUCTION

## *Statement of the Problem*

One of the most serious waste management problems in Florida concerns the huge stockpiles of by-product gypsum produced by the phosphate industry. In fact, the phosphate industry, as it operates in Florida as well as in many other parts of the world, could more accurately be termed a “gypsum” industry. During the wet process manufacture of phosphoric acid, the basic raw material from which most phosphatic fertilizers are made, concentrated phosphate rock is reacted with sulfuric acid which results in the production of substantial quantities of by-product gypsum known as “phosphogypsum.” A simplified chemical reaction for this process may be shown as follows:



While the mole ratio between gypsum and phosphoric acid is 5:3, the mass ratio is about 3:1, *i.e.*, about 3 tons of gypsum are produced for every ton of acid. Phosphogypsum produced during this process is filtered off and pumped as a slurry to nearby storage areas, the so-called “gyp-stacks.” The phosphate industry in Florida produces approximately 30 million metric tons of by-product gypsum per year, and the inventory within the state is projected to reach about 1 billion metric tons by the year 2000.

Although phosphogypsum is used in some countries for production of cement and other construction materials, its commercial use in the U.S. is currently limited to small quantities sold to farmers as a soil amendment. This restriction was developed because of the impurities contained in phosphogypsum, especially



radium and other radionuclides derived from the uranium-rich phosphate rock. The Environmental Protection Agency (EPA), acting under NESHAP (National Emission Standards for Hazardous Air Pollutants) and stimulated by concern for radon emissions from phosphogypsum, ruled that gypsum must be placed on stacks or mine cuts and that only gypsum containing less than 10 pCi/g  $^{226}\text{Ra}$  can be removed for agricultural purposes.

Besides the obvious waste of a potentially valuable by-product and the unsightly physical appearance of the stockpiles, the main problem associated with phosphogypsum storage is the potential effect on the surrounding environment, specifically the air and water resources in, the vicinity of gypsum stacks (Kouloheris, 1980). Studies that have considered the radiological aspects of the agricultural use of phosphogypsum have generally concluded that the increased risk is low, both from the increased radon flux from the soil and from uptake by plants (Lindeken and Coles, 1978; Lindeken, 1980; Roessler, 1984; Roessler, 1988). The most important pathway between phosphogypsum-derived radionuclides and humans, therefore, is probably through groundwater contamination associated with gypsum stacks (Miller and Sutcliffe, 1984).

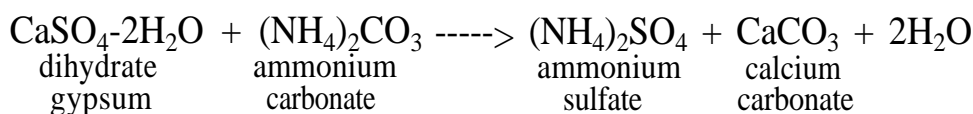
Can anything be done about this wasteful and potentially environmentally damaging situation? Many suggestions have been made including: (1) use of phosphogypsum for road beds; (2) recovery of elemental sulfur either chemically or microbially; and (3) direct agricultural application. At present, there does not appear to be a high degree of confidence that any of these approaches will be successful in terms of large-scale volume reduction. We feel that an important question to ask at this point is whether phosphogypsum can be radiochemically purified or converted to another form without the associated radionuclides in a cost



effective manner. Can large-scale radiochemical purification be done economically? Perhaps, especially if combined with a process that will also result in an economically-attractive product. One possibility for such a process is the large-scale conversion of phosphogypsum to the two end products (calcium carbonate and ammonium sulfate) of the so-called “Merseberg” ammonocarbonation reaction. One of these products, ammonium sulfate, is an excellent fertilizer that adds both sulfur and nitrogen to the soil. The other reaction product, calcium carbonate, could be used for neutralizing acidic process waters associated with the phosphate industry, or calcined to drive off the CO<sub>2</sub> which could be recycled for the production of the ammonium carbonate needed in the Merseberg process.

***Description of the Merseberg Process***

The manufacture of ammonium sulfate, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, from gypsum (or anhydrite) is a very old technology, first developed by I.G. Farben Industries prior to 1914 (Gopinath, 1968). According to Sacher (1968), it was actually in use in Vienna as early as 1809 although not applied on an industrial scale until after the development of ammonia synthesis during World War II. Any type of gypsum, including by-product phosphogypsum, may be reacted with ammonium carbonate to form ammonium sulfate and calcium carbonate by the Merseberg process. Chemically, this process may be represented by the following reaction:



Using pure gypsum, the ammonocarbonation reaction has a high equilibrium constant (K = 4820 @25°C with 0.125N (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>; Chen, 1990) and the equilibrium conversion of calcium sulfate can reach 99.97%. Because of

impurities such as silica sand, organic matter and phosphate, phosphogypsum has a lower conversion efficiency but still displays satisfactory performance with reaction kinetics on the order of 1 hour and conversions of about 97% (conversions up to 99% were observed when hemihydrate was used; Gopinath, 1968).

When by-product gypsum is used in the Merseberg process, the gypsum from the wet-process phosphoric acid plant is “purified” by washing with water and then treated with ammonium carbonate solution which, results in a slurry of calcium carbonate in an ammonium sulfate solution. The ammonium carbonate solution is made from liquid ammonia and carbon dioxide which can be derived from a variety of sources. After separation of the calcium carbonate, any excess ammonium carbonate is neutralized with sulfuric acid, the ammonium sulfate solution is concentrated, and ammonium sulfate is crystallized. Several variations on this overall approach are possible, and modifications have been made to suit the needs of a particular market. For example, instead of crystallizing the ammonium sulfate, it can be retained as a liquid for further processing into various mixed fertilizers such as ammonium sulfate phosphate. A flowchart for the industrial-scale Merseberg process (Fig. 1) illustrates some of the process factors, which have been recognized as relating to the general quality and efficiency of ammonocarbonation (Gopinath, 1968): (1) quality of the phosphogypsum; (2) particle size; (3) concentration of ammonium carbonate; (4) conversion of calcium sulfate; (5) filtration of  $\text{CaCO}_3$ ; and (6) evaporation and crystallization.

### ***Research Objectives***

The main purpose of this investigation was to determine the pathways of  $^{226}\text{Ra}$  and associated radionuclides during the conversion of phosphogypsum to ammonium sulfate by the Merseberg process. Since there is no U.S. production at

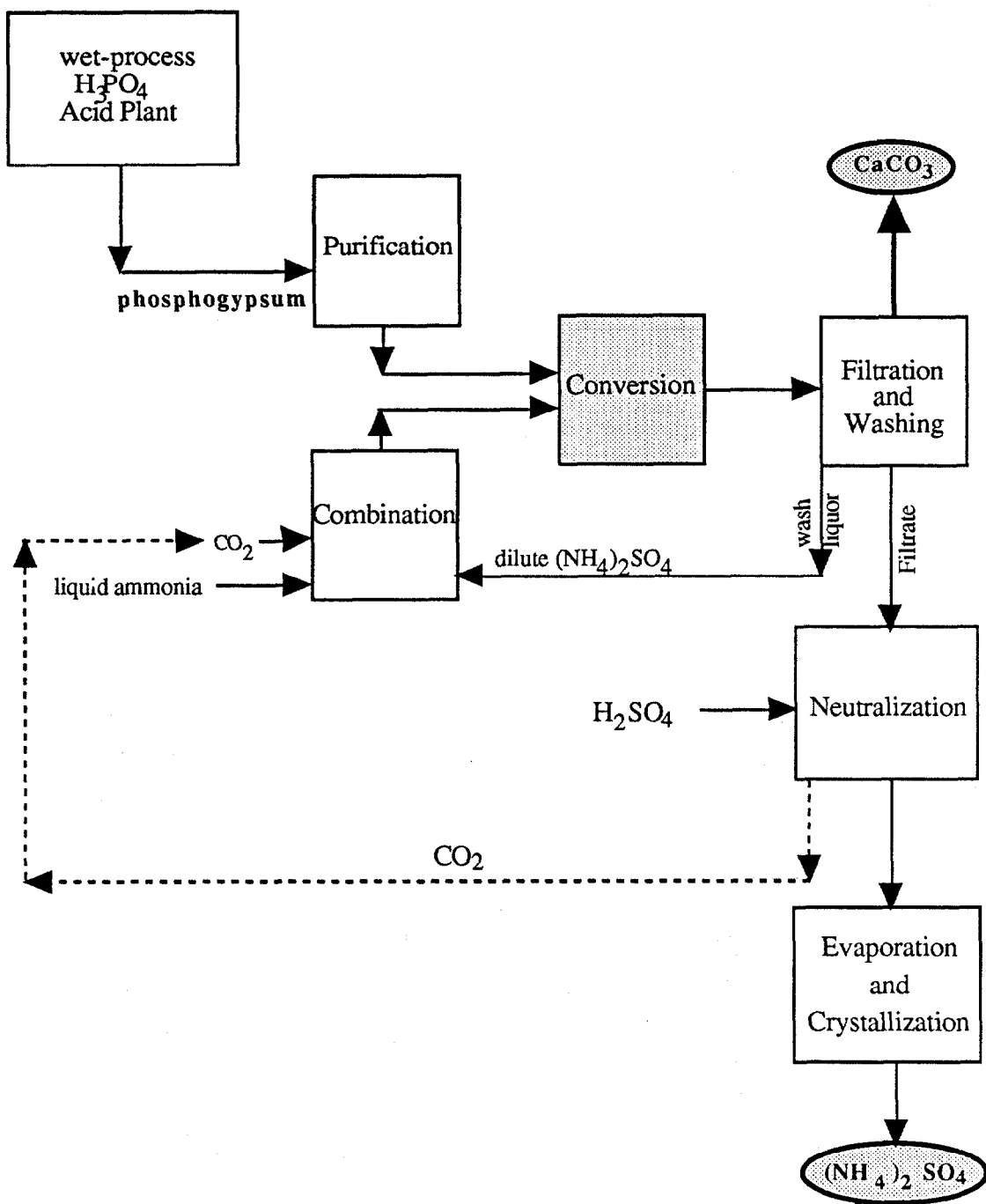


Figure 1 Simplified flow chart of the industrial-scale Merseberg process.

present, the assessment of radionuclide behavior was performed on samples received from plants operating in Asia. As far as we can determine, our data represent the only documented results for radionuclides contained in products from the Merseberg process.

## **MATERIALS AND METHODS**

The approach we used in this study was to analyze the phosphate ore rock, the feed phosphogypsum, and the end products of the reaction from industrial-scale ammonocarbonation plants already in operation. Samples were received and analyzed from three active Merseberg-process plants in Asia: (1) Gresik, Indonesia; (2) Anhui, China; and (3) Vadodara, India. In addition, similar samples were used which were received from a laboratory-scale operation at a research institute in Cairo, Egypt.

Since water exists in phosphogypsum in both a combined and a free form, consideration must be given to the methodology of drying these types of samples before analysis. Free water is difficult to remove completely by air drying samples at room temperature because the sample is influenced by humidity. Furthermore, we observed by x-ray diffraction (XRD) procedures that dihydrate gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) can be partially converted into hemihydrate ( $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ ) even at relatively low temperatures ( $<60^\circ \text{C}$ ) in a drying oven. Since phase changes between these two forms cannot be perfectly controlled and there exists a potential mass difference of greater than 15% between dihydrate and hemihydrate, analyses of phase mixtures would result in unacceptable and irreproducible artifacts. All gypsum samples were prepared, therefore, by drying to a constant weight in a

vacuum desiccator at room temperature. XRD analysis subsequent to drying selected samples confirmed that dihydrate was the only significant  $\text{CaSO}_4$  phase present. Thus, all bulk radiochemical analyses of phosphogypsum are reported on a dihydrate, moisture-free basis.

Activities of  $^{238}\text{U}$ ,  $^{226}\text{Ra}$ , and  $^{210}\text{Pb}$  were determined by high-resolution gamma spectrometry. Samples were homogenized after drying and packed into 100-cc aluminum cans which were then hermetically sealed. Activities of  $^{238}\text{U}$  were obtained from the 63.2 keV photopeak associated with its direct  $^{234}\text{Th}$  daughter while  $^{210}\text{Pb}$  was assessed from its direct photopeak at 46.5 keV. Differences in self-absorption between samples and calibration standards for these low-energy photopeaks were evaluated using a correction based on direct transmission measurements (Cutshall *et al.*, 1983; Burnett *et al.*, 1993). The activities of  $^{226}\text{Ra}$  were determined by taking the average activities based on three separate photopeaks of 2 radon daughters:  $^{214}\text{Pb}$  at 295.2 keV and 351.9 keV, and  $^{214}\text{Bi}$  at 609.3 keV. Samples were all stored after sealing in the aluminum cans for sufficiently long periods of time (~3 weeks) to ensure secular equilibrium between  $^{222}\text{Rn}$  and its parent  $^{226}\text{Ra}$ . The high-purity germanium detector used was calibrated by reference to a series of NIST and EPA natural soil and rock standards.

Isotope dilution alpha spectrometry was used to determine quantitatively the activities of  $^{210}\text{Po}$ . Chemical yields were determined by the addition of a known activity tracer,  $^{209}\text{Po}$ . For each analysis, an accurately weighed portion of the same dried and ground sample as used for the gamma spectrometry measurement was put into an acid digestion bomb with tracer and concentrated  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{HF}$ , and  $\text{HClO}_4$  acids and allowed to digest overnight at approximately  $160^\circ\text{C}$ . The sulfate

phases were then converted to the more soluble carbonate form by reaction with potassium carbonate (Burnett and Tai, 1992). Prepared sources were counted in alpha spectrometers which had their backgrounds maintained at very low levels (on the order of <0.005 cpm under single peaks) by an alpha recoil prevention system based on a critical air thickness and a small (~6 volt) negative potential applied to the source holder (Sill and Olson, 1970). Data reduction was performed by customized computer programs that included provisions for decay corrections and error propagation due to counting statistics and other sources of error.

## RESULTS AND DISCUSSION

### *Radiochemical Results*

China: Two sets of samples were received for analysis from the Shanghai Research Institute in China. The first set of samples (referred to here as Group A) consisted of phosphogypsum manufactured from Keiyan phosphate rock, samples of the phosphate ore itself, and ammonium sulfate and calcium carbonate produced from the phosphogypsum. This initial sample group was divided into two sets of subsamples to evaluate the homogeneity of the material. The second set (Group B) consisted of ammonium sulfate manufactured in a plant in the Anhui Province of China from Yichang phosphate (Hubei province). The phosphogypsum in this sample group was reported to have been produced from the manufacture of wet process phosphoric acid in a 30 metric ton  $P_2O_5$ /day installation. The ammonium sulfate produced from this gypsum had a slight greenish color and smaller than normal crystal size, perhaps due to a corroded stainless steel evaporator pan caused by elevated acidity.

The radiochemical results for the China samples show that both the Keiyan and the Yichang phosphate rock are unusually low in uranium and radioactive daughters (**Table 1**). Uranium activities of 50 dpm/g and higher are common in most phosphate deposits, including those in Florida (Burnett, 1988). In spite of the low activities in the ore rock and by-product gypsum from China, it is clear that radium and its daughters favor the calcium carbonate product of the Merseberg process and the ammonium sulfate is extremely low in radioelements. Note that uranium is rarely high in phosphogypsum since it tends to favor the phosphoric acid phase during the chemical processing.

Indonesia: One group of samples of phosphogypsum, ammonium sulfate, and calcium carbonate were received from a plant in Gresik, Indonesia (PT Petrokimia Gresik). Unfortunately, we received only one set of samples because their ammonium sulfate plant went out of operation in August, 1993, reportedly because of a lack of CO<sub>2</sub>. The company indicated to us that they plan to open a new ammonium sulfate plant in the near future. We split the single group of samples received from Indonesia into two subsets and analyzed them separately for radionuclides. The results (**Table 2**) show that the Indonesian phosphogypsum is more typical in its radiological character than that examined from China. Both subsamples show that the gypsum is low in uranium (<3 dpm/g) with higher and comparable activities of <sup>226</sup>Ra, <sup>210</sup>Pb, and <sup>210</sup>Po (all ~28 dpm/g). Unfortunately, we were not able to obtain a sample of the phosphate ore which produced the phosphogypsum nor could we obtain information about its origin. The primary interest here, however, is that the data indicates that the radioelements associated with phosphogypsum report mainly to the calcium carbonate rather than to the ammonium sulfate fraction. Radium and its daughters are all 0.5 dpm/g or less in the ammonium sulfate product. Uranium, lowest of all the radionuclides examined



Table 1. Radiochemical results for samples from Shanghai Research Institute, Shanghai, China. All results reported in dpm/g and errors quoted are  $\pm 1\sigma$  based on counting statistics.

Sample	$^{238}\text{U}$	$^{226}\text{Ra}$	$^{210}\text{Pb}$	$^{210}\text{Po}$
<i>Group A #1</i>				
Keiyan phosphate rock	$9.1 \pm 0.3$	$7.4 \pm 0.1$	$10.3 \pm 0.3$	$7.5 \pm 0.2$
phosphogypsum	$0.9 \pm 0.1$	$5.1 \pm 0.1$	$4.9 \pm 0.2$	$4.9 \pm 0.2$
ammonium sulfate	$0.1 \pm 0.1$	$0.04 \pm 0.01$	$0.1 \pm 0.1$	$0.020 \pm 0.004$
calcium carbonate	$1.2 \pm 0.1$	$8.4 \pm 0.2$	$7.9 \pm 0.2$	$7.2 \pm 0.2$
<i>Group A #2<sup>a</sup></i>				
Keiyan phosphate rock	$5.6 \pm 0.7$	$6.1 \pm 0.5$	$4.3 \pm 0.7$	$8.4 \pm 0.2$
phosphogypsum	$1.2 \pm 0.3$	$4.98 \pm 0.03$	$4.7 \pm 0.3$	$4.9 \pm 0.2$
ammonium sulfate	<0.2	$0.06 \pm 0.04$	<0.2	$0.02 \pm 0.01$
calcium carbonate	$0.6 \pm 0.3$	$8.2 \pm 0.2$	$8.0 \pm 0.4$	$7.2 \pm 0.2$
<i>Group B #1</i>				
Yichang phosphate rock	$3.0 \pm 0.8$	$2.6 \pm 0.5$	$1.6 \pm 0.7$	$3.0 \pm 0.1$
phosphogypsum	<1.5	$2.5 \pm 0.4$	<1.1	$2.5 \pm 0.1$
ammonium sulfate	<1.8	<0.4	<1.3	$0.011 \pm 0.002$
calcium carbonate	<1.7	$5.4 \pm 0.3$	$1.9 \pm 0.9$	$5.4 \pm 0.1$

<sup>a</sup>Separate aliquot of sample reported as "Group A #1".

in the phosphogypsum is actually somewhat higher (~1 dpm/g) than the other radionuclides in the ammonium sulfate. This is still a very low concentration, equivalent to what may be found in many typical soils.

Table 2. Radiochemical results for samples from P.T. Petrokima Gresik, Indonesia. All results reported in dpm/g and errors quoted are  $\pm 1\sigma$  based on counting statistics.

Sample	$^{238}\text{U}$	$^{226}\text{Ra}$	$^{210}\text{Pb}$	$^{210}\text{Po}$
<i>Group A #1</i>				
phosphogypsum	$2.6 \pm 0.3$	$28.4 \pm 0.2$	$28.8 \pm 0.5$	$26.7 \pm 0.6$
ammonium sulfate	$0.9 \pm 0.1$	$0.52 \pm 0.04$	$0.2 \pm 0.1$	$0.09 \pm 0.02$
calcium carbonate	$5.9 \pm 0.5$	$43.8 \pm 0.2$	$48.1 \pm 0.8$	$36.2 \pm 0.5$
<i>Group A #2<sup>a</sup></i>				
phosphogypsum	$2.7 \pm 0.7$	$27.5 \pm 0.2$	$28.4 \pm 0.8$	$28.5 \pm 0.2$
ammonium sulfate	$1.2 \pm 0.1$	$0.53 \pm 0.04$	<0.3	$0.11 \pm 0.02$
calcium carbonate	$3.3 \pm 0.7$	$39.3 \pm 0.2$	$43.3 \pm 0.8$	$38.5 \pm 0.9$

<sup>a</sup>Separate aliquot of sample reported as "Group A #1".

India: Two groups of samples were sent to us from the Gujarat State Fertilizer Company (GSFC) Ltd. in Vadodaro, India. The original shipment ("Group A"), sampled in August, 1993, was divided into 3 subsets and analyzed separately. The second shipment ("Group B"), sent to us in June, 1994, was analyzed as a single set. The GSFC phosphogypsum is a by-product of the wet process dihydrate production of phosphoric acid from phosphate ore imported from Senegal. The by-product calcium carbonate from the ammonium sulfate plant is made in a slurry and neutralized with acid from the phosphoric acid plant in large, open ponds. The dried calcium carbonate is reclaimed and stockpiled for disposal.

GSFC started operation of an ammonium sulfate plant based on the Merseberg process in 1967 with an initial capacity of 470 metric tons/day. In the last five

years, the plant has increased its production to an average of 600 mtpd, about 500 mtpd *via* the Merseberg process and approximately 100 mtpd by a direct neutralization (DN) process which was added to the plant in 1969. In the DN process pure ammonia vapor is neutralized with sulfuric acid in the evaporators/crystallizers along with the ammonium sulfate liquor produced from the Merseberg process. The resulting ammonium sulfate is thus of “mixed” origin, with about 16% being contributed from the DN process. The second group of samples sent to us for analysis contained ammonium sulfate samples that were collected in three different ways: (1) mixed Merseberg + DN collected wet in a centrifuge; (2) mixed Merseberg + DN dry composite of evaporated crystals; and (3) Merseberg process only. The first two samples were reported to consist of about 20% ammonium sulfate from the DN process.

The results from our radiochemical analyses show that the three subsamples of Group A contain nearly identical activities in all the phases analyzed (**Table 3**). The material thus appears to be very homogeneous, especially on the scale of the sample size used for the  $\gamma$ -ray spectrometric determinations ( $\sim 100 \text{ cm}^3$ ). The Group B samples, collected from the plant approximately one year later, also show very similar results for the Senegal phosphate rock, phosphogypsum, and calcium carbonate. All of the ammonium sulfate samples (3 replicates from Group A and the 3 separate samples in Group B) from this plant are very low in radionuclides compared to the other materials analyzed. There does not appear to be a discernible difference reflected in the analysis as a result of the chemical process used. The two ammonium sulfate samples, which contain about 20% DN process material, have nearly the same activities of  $^{238}\text{U}$ ,  $^{226}\text{Ra}$ , and  $^{210}\text{Pb}$  as the sample produced solely by the Merseberg process (Group B, ammonium sulfate #3).

Table 3. Radiochemical results for samples from Gujarat State Fertilizer Company, Vadodaro, India. All analyses reported as dpm/g and errors quoted are  $\pm 1s$  based on counting statistics.

Sample	$^{238}\text{U}$	$^{226}\text{Ra}$	$^{210}\text{Pb}$	$^{210}\text{Po}$
<i>Group A #1</i>				
Senegal phosphate	67 $\pm$ 1	54.5 $\pm$ 0.3	68 $\pm$ 3	53.7 $\pm$ 0.7
phosphogypsum	3.6 $\pm$ 0.4	30.6 $\pm$ 0.2	30 $\pm$ 1	25.1 $\pm$ 0.6
ammonium sulfate	1.1 $\pm$ 0.1	0.82 $\pm$ 0.03	0.10 $\pm$ 0.06	0.09 $\pm$ 0.02
calcium carbonate	4.7 $\pm$ 0.9	45.6 $\pm$ 0.2	48.0 $\pm$ 1	37.1 $\pm$ 0.3
<i>Group A #2<sup>a</sup></i>				
Senegal phosphate	68.8 $\pm$ 0.7	54.0 $\pm$ 0.3	67.8 $\pm$ 0.7	55 $\pm$ 1
phosphogypsum	1.8 $\pm$ 0.4	30.6 $\pm$ 0.3	29.0 $\pm$ 0.5	25.1 $\pm$ 0.5
ammonium sulfate	1.0 $\pm$ 0.1	0.76 $\pm$ 0.01	<0.3	0.13 $\pm$ 0.02
calcium carbonate	2.5 $\pm$ 0.5	44.9 $\pm$ 0.6	50.7 $\pm$ 0.5	34.1 $\pm$ 0.6
<i>Group A #3<sup>a</sup></i>				
Senegal phosphate	69 $\pm$ 1	53.7 $\pm$ 0.2	70 $\pm$ 1	56.3 $\pm$ 0.7
phosphogypsum	<0.6	30.3 $\pm$ 0.2	29.7 $\pm$ 0.6	27.0 $\pm$ 0.3
ammonium sulfate	1.1 $\pm$ 0.1	0.72 $\pm$ 0.03	<0.3	0.09 $\pm$ 0.02
calcium carbonate	3.5 $\pm$ 0.9	45.4 $\pm$ 0.3	51 $\pm$ 1	41.4 $\pm$ 0.9
<i>Group B #1<sup>a</sup></i>				
Phosphate Ore	71.0 $\pm$ 0.8	56.2 $\pm$ 0.6	70.6 $\pm$ 0.9	59.4 $\pm$ 0.6
Phosphogypsum	3.3 $\pm$ 0.5	32.4 $\pm$ 0.3	35.6 $\pm$ 0.5	33.6 $\pm$ 0.4
Calcium Carbonate	4.2 $\pm$ 0.6	47.9 $\pm$ 0.6	54.0 $\pm$ 0.7	46.1 $\pm$ 0.7
Ammonium Sulfate - 1 <sup>c</sup>	0.3 $\pm$ 0.1	1.21 $\pm$ 0.03	<0.3	0.22 $\pm$ 0.01
Ammonium Sulfate - 2 <sup>c</sup>	0.5 $\pm$ 0.1	1.05 $\pm$ 0.03	<0.3	0.16 $\pm$ 0.01
Ammonium Sulfate - 3 <sup>c</sup>	0.5 $\pm$ 0.1	0.86 $\pm$ 0.02	<0.2	0.19 $\pm$ 0.01

<sup>a</sup>Seperate aliquot from same sample repeated as "Group A #1"

<sup>b</sup>Different set of samples collected approximately 1 year after "Group A"

<sup>c</sup> 1 = Merseberg + DN process, collected wet in centrifuge

2 = Merseberg + DN process, dry composite of evaporated crystals

3 = Merseberg process only

Egypt: In addition to the samples discussed above, all collected from operating commercial-scale ammonium sulfate plants, we also received a set of samples from a research laboratory at the National Research Center in Cairo, Egypt. These samples were produced in the laboratory from Nile Valley and Red Sea phosphate rock samples. The only phosphogypsum sample received was produced from the Nile Valley rock. The two calcium carbonate samples (B1 and B2) were both manufactured from the same materials, but sample “B1” was produced through reaction of phosphogypsum with gaseous  $\text{NH}_3$  and  $\text{CO}_2$  rather than aqueous ammonium carbonate as the case of “B2”.

The radiochemical data for the Egyptian samples (**Table 4**) indicate that there are some minor differences between the two different carbonate samples with the sample produced by gaseous  $\text{NH}_3$  and  $\text{CO}_2$  somewhat lower in radium and daughters but higher in uranium. These differences, however, could be due to slight variations caused by the observed heterogeneity of these samples. Note, for example, that the replicate analyses of the phosphogypsum sample did not produce results as consistent as seen for replicates from the Asian plants. The results concerning the purity of the ammonium sulfate are basically the same as seen for the other sample groups with very low levels for all radionuclides investigated.

### ***Radium Budget***

It is clear from the data presented above that the radionuclides that concentrate in phosphogypsum report mainly to the calcium carbonate phase during the ammonocarbonation process. To illustrate the quantitative extent of this transfer, it is instructive to consider this in terms of a mass balance. We will use radium to demonstrate. Should all the  $^{226}\text{Ra}$  originally contained in “pure” phosphogypsum be transferred quantitatively to calcium carbonate, one may estimate the final

Table 4. Radiochemical results for samples from the National Research Center in Cairo, Egypt. All results reported dpm/g and errors quoted are  $\pm 1\sigma$  based on counting statistics.

Sample	$^{238}\text{U}$	$^{226}\text{Ra}$	$^{210}\text{Pb}$	$^{210}\text{Po}$
Nile Valley phosphate B2	$50 \pm 2$	$35.3 \pm 0.5$	$34 \pm 1$	$28.9 \pm 0.2$
Rea Sea phosphate C	$32 \pm 1$	$31 \pm 1$	$26.1 \pm 0.9$	$37.7 \pm 0.7$
phosphogypsum B2	$6 \pm 2$	$26.7 \pm 0.3$	$26 \pm 2$	$25.6 \pm 0.1$
phosphogypsum B2/2	$4 \pm 1$	$22.3 \pm 0.5$	$20 \pm 1$	$25.5 \pm 0.3$
ammonium sulfate B1	$<2.1$	$<0.7$	$<1.5$	$0.03 \pm 0.01$
ammonium sulfate B2	$<2.1$	$<0.4$	$<1.5$	$0.013 \pm 0.004$
calcium carbonate B1	$7 \pm 1$	$19 \pm 1$	$16 \pm 1$	$23.7 \pm 0.3$
calcium carbonate B2	$4 \pm 1$	$23.1 \pm 0.4$	$22.9 \pm 0.8$	$25.0 \pm 0.3$

activity in the calcium carbonate by accounting for the differences in molecular weights between the two phases (mol.wt.  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} = 175$ ; mol. wt.  $\text{CaCO}_3 = 100$ ). Thus, assuming that we are dealing with pure phases, a quantitative transfer from dihydrate gypsum to calcium carbonate would result in the carbonate phase being 1.75 times more concentrated in  $^{226}\text{Ra}$  than the gypsum. It should be emphasized, however, that the actual materials in question are not pure. Typical phosphogypsum samples contain 5-10% impurities in the form of silica sand, organic material, and other components.

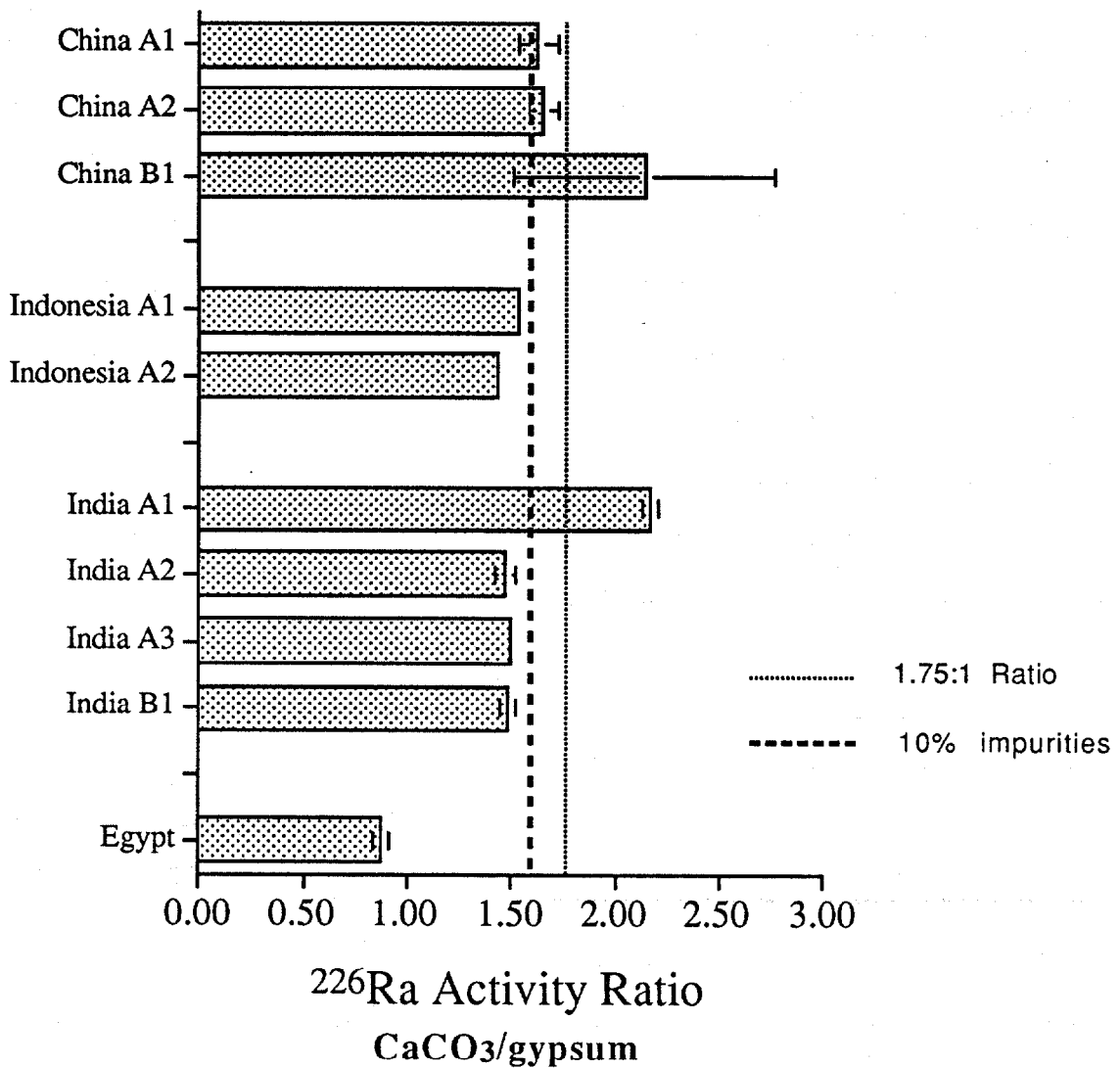
The observed radium-in-carbonate to radium-in-gypsum ratios in the samples reported here are either within analytical error of the ideal value (1.75) or lower (**Fig. 2**). If we assume that only 90% of the phosphogypsum reacts (allowing for 10% impurities) and that the calcium carbonate which precipitates is pure, the calculated ratio decreases to 1.58, very close to that observed in most of these samples. Only the samples from Egypt, which were known to have larger quantities of impurities, were distinctly different. An XRD scan of the calcium carbonate fraction, for example, showed that there remained a significant amount of unreacted gypsum.

### ***Agricultural and Economic Considerations***

Need for Ammonium Sulfate: The expanding role of sulfur in accelerating crop production, especially in tropical countries, has become more widely recognized in the last few years. Sulfur is an essential nutrient for plants and it contributes to increased crop yields both by providing a direct nutritive value and by improving the efficiency with which plants use other essential nutrients, especially nitrogen and phosphorus. Several studies have shown that plant uptake of sulfur is often as great or greater than the amount of phosphorus removed from the soil (Kanwar and Mudahar, 1986).

Fertilizer is only one source, albeit an important one, of the sulfur supplied to soils. Additionally, not all sulfur added to soil is utilized by plants. A large share may leach out or may become fixed in the soil in a form unavailable to plants. The relative importance of the various sources of sulfur varies with locality, level of industrialization, environmental considerations, and stage of economic development.





**Figure 2** Ratio of  $^{226}\text{Ra}$  activity in  $\text{CaCO}_3$  to  $^{226}\text{Ra}$  in phosphogypsum. If all the radium initially in the by-product gypsum was quantitatively transferred to the  $\text{CaCO}_3$ , the activity ratio would be 1.75. If the gypsum contained 10% unreactive impurities, the resulting ratio would be somewhat lower as indicated by the heavy dashed line.

During the last two decades, changes in agricultural practices and fertilizer manufacture have had a major impact on sulfur availability. “Green Revolution” technology, with corresponding increases in crop yields and multiple cropping, will continue to increase demands for sulfur. The aggregate sulfur availability to agricultural soils, on the other hand, has been declining over the last several years for 3 reasons: (1) many countries never had any policy of supplying sulfur to soil (although it was applied inadvertently *via* the use of fertilizer that also contained sulfur); (2) the fertilizer industries have been replacing sulfur-containing fertilizers (as ammonium sulfate) with sulfur-free fertilizers (as urea) because of high distribution costs and the perception that sulfur itself was of little importance; and (3) the environmental concern for cleaner air has reduced the supply of sulfur (as “acid rain”) from the atmosphere (Kanwar and Mudahar, 1986).

Thus, we are now facing a serious “sulfur gap” in many areas. Although sulfur deficiencies in soil are not always easy to recognize, there is a growing body of evidence that the lack of sulfur is often responsible for lower productivity. It has been observed, for example, that tea farmers in Nepal and Sri Lanka and tobacco growers in India produce better yields when using ammonium sulfate rather than urea (S. Ahmed, *pers. comm.*). In general, the situation is that while higher crop yields require more sulfur, the actual trend is of a decreasing sulfur supply as a result of lower levels of inadvertent addition and atmospheric pollution. Consequently, sulfur deficiency problems in soils are now becoming widespread.

The situation in India dramatically illustrates this problem. Aggregate nutrient ( $N+P_2O_5+K_2O$ ) consumption in India increased from 66,000 metric tons in 1951/52 to 5.5 million metric tons in 1980/81 (FAO, 1983). Yet due to changing sources of fertilizer over this time period, the estimated share of sulfur in

the total nutrient consumption dropped from 54% in 1951/52 to 34% in 1965/66 and to only 5% in 1980/81.

Sulfur deficiencies are clearly not limited to soils in the developing world. Sulfur deficiencies for plant growth have now been reported in over 35 states in the U.S., including Florida, where the coarse textured soils apparently exhibit sulfur depletion because of low organic matter levels and leaching. A pair of 3-year experiments in Arcadia and Pensacola demonstrated that sulfur application significantly increased both the yield and quality of forage grass pasture (Rechcigl, 1991; 1992a; 1992b). These tests were conducted by treatment of test plots with two different forms of nitrogen, ammonium nitrate and ammonium sulfate. The highest yields were invariably obtained with ammonium sulfate rather than the ammonium nitrate. The results showed that sulfur addition can increase production of harvested forages such as bahia grass by as much as 25%. This is a meaningful finding as bahia grass is an important forage crop grown in Florida, with nearly 2.5 million acres farmed annually. In addition to the increased yields, the quality of the forage crop was improved when ammonium sulfate was added to the soil. Quality in this case is evaluated by an increased protein content and improved digestibility of the grass. Thus, sulfur addition, such as in the form of ammonium sulfate, appears to be necessary for maximum production and quality of bahia grass and other crops.

Outlook: We thus find ourselves in a situation where two significant, yet seemingly unrelated, problems co-exist. One of these problems (phosphogypsum waste) has both industrial and environmental ramifications while the other (sulfur deficiency) is strictly agricultural. Although both of these problems have significant economic and social impact, they are not often considered in the same

context. Yet, there may well be a common solution to both of these problems -- the use of phosphogypsum to manufacture ammonium sulfate fertilizer.

Production of ammonium sulfate from phosphogypsum continues to this day in parts of Asia. The analytical results presented in this report from samples from these plants show that the radioelements which concentrate in phosphogypsum do not report to the ammonium sulfate product. Furthermore, it has been demonstrated over several years that the production can be done economically, at least within the economies of some Asian countries (Gopinath, 1968; Ellwood, 1968; Butler, 1969; Kasturirangan, 1968; Ramachandran *et al.*, 1992).

However, one reason that the Merseberg process can be economically realized in India and some other countries is because sulfur is in short supply there and has to be imported. The availability of by-product gypsum, therefore, provides an inexpensive raw material for producing a sulfur-containing fertilizer. In countries like the U.S., where the availability of sulfur resources is not an issue, the principal economic problems lie with the relatively low nitrogen content of ammonium sulfate and the availability of ammonium sulfate from other sources. Since  $(\text{NH}_4)_2\text{SO}_4$  contains only 21% N while urea contains 46% N, the production and subsequent transport costs per unit nitrogen is obviously higher for ammonium sulfate. Fertilizer manufacturers have thus tended to favor the so-called “high analysis” fertilizers (note that “high analysis” here refers to content of nitrogen or phosphorus, not sulfur ). In spite of this apparent cost disadvantage, the prospect of being able to provide sulfur as well as nitrogen to soil to overcome the sulfur deficiency problems referred to earlier and to address the problem of phosphogypsum disposal in the phosphate industry has great practical appeal.

Commercial-scale production of ammonium sulfate has not been considered economically feasible in Florida because the price has been kept low due to the by-product production of ammonium sulfate from other industries. Most ammonium sulfate today is a co-product from the manufacture of the nylon intermediate-caprolactum. The U.S., now the leading ammonium sulfate producer, accounts for 75% of its product *via* caprolactum. New technologies which have developed recently have lowered the amount of ammonium sulfate to product ratio from 5:1 to about 1.3:1. In addition, BASF is said to be developing a method for recycling carpets for nylon that wouldn't produce any ammonium sulfate at all. Thus, the demand has been improving over the last few years as the sulfur requirements are recognized and the main supply *via* caprolactum production may be diminishing. These trends have produced a relatively steady increase in the world ammonium sulfate prices over the last three to four years (Anonymous, 1994).

The current phosphogypsum situation in Florida is unfortunate, as the practice of stockpiling is unattractive from many points of view. Not only are the gypsum stacks unsightly and present a possible environmental problem, but they will require long-term expenditures for maintenance and monitoring. A "pass-through" technology, which would convert the waste product to a useful commodity is clearly a more efficient use of our resources. After all, we now use sulfur (as  $H_2SO_4$ ) to convert another nutrient, phosphorus, into a form suitable for soil application. Each sulfur atom is thus used only once and is converted to by-product gypsum which is subsequently stockpiled. However, if we started producing ammonium sulfate from by-product gypsum, each sulfur atom would be used twice: once in the production of phosphoric acid and again for manufacture of ammonium sulfate, an excellent fertilizer. In addition, various uses exist for the by-product  $CaCO_3$  formed during the ammonocarbonation reaction. One

possibility would be to convert the  $\text{CaCO}_3$  to lime ( $\text{CaO}$ ) and recycle the liberated  $\text{CO}_2$  back into the Merseberg process for production of the ammonium carbonate. Significant amounts of  $\text{CaCO}_3$  could also be used by the phosphate industry to buffer various acidic processes waters.

The stoichiometry of the ammonocarbonation process is such that about 30% more gypsum is consumed than ammonium sulfate produced. While it is not our intention here to present arguments in support of the economic feasibility of developing an ammonocarbonation enterprise in Florida or other regions where phosphogypsum is produced, the following points would appear to make such an undertaking logical and attractive: (1) fully-developed fertilizer infrastructures are already in place in these areas; (2) the gypsum is readily available; and (3) agricultural specialists are recommending addition of sulfur, as well as nitrogen and phosphorus, in many cases. Unfortunately, large-scale conversion of phosphogypsum cannot become economically viable until uses are in place for the additional ammonium sulfate and calcium carbonate. Long-term storage of ammonium sulfate could result in groundwater contamination and decreases the quality of the product (it tends to become very hard). Stockpiling large amounts of calcium carbonate requires large areas because the angle of repose of the material is so small. It is thus very important that the demand for these products be adequate to ensure keeping pace with the projected production.

If one takes the optimistic view that there would be sufficient demand, ammonocarbonation could reduce and eventually eliminate the significant construction and maintenance costs associated with gypsum stacks, estimated to be in excess of several million dollars per year. Now that the State of Florida has decided to “close” inactive and unlined gypsum stacks within the next several

years, there are new costs to consider. Schultz (1992) estimated that if all the gypsum stacks in the U.S. had to be closed by covering with an impervious membrane and a soil cap to support vegetation, the cost would be in the neighborhood of U.S. \$1.3 billion or an average of \$20 million per stack! Furthermore, these cost estimates do not include the on-going costs of environmental monitoring. It thus seems appropriate to review our strategies in terms of dealing with this waste. Additional research should be encouraged to find a cost-effective means to reprocess phosphogypsum. Conversion to a useful product, even without a significant profit margin, should be preferable to the huge expense and endless monitoring required for environmental isolation.

## **SUMMARY**

Samples from commercial-scale ammonium sulfate plants in China, Indonesia, and India, together with a similar sample set from a research laboratory in Egypt, have been analyzed to evaluate the flow of radioelements during the ammonocarbonation (Merseberg process) conversion of phosphogypsum to ammonium sulfate. Results showed that while concentrations of uranium and radioactive daughter products vary in the phosphate rock samples (and thus in the resulting phosphogypsum), the sample sets displayed similar trends and indicate that the radionuclides that originally concentrate in the phosphogypsum ( $^{226}\text{Ra}$ ,  $^{210}\text{Pb}$ , and  $^{210}\text{Po}$ ) all concentrate in the by-product calcium carbonate. The resulting ammonium sulfate is thus very low in radionuclides, lower than found in most natural materials. A review of the relevant agricultural literature reveals that ammonium sulfate is an excellent fertilizer for many crops and could help alleviate the “sulfur gap” which has been documented in many agricultural areas. While



encouraging in terms of use as a fertilizer, large-scale production of ammonium sulfate in order to provide relief for the “phosphogypsum problem” has been seriously hampered by economic considerations. The abundant supplies of ammonium sulfate as a co- or by-product from other industries may be decreasing and thus encourage investment in ammonium sulfate production from phosphogypsum.

## **ACKNOWLEDGMENTS**

We sincerely thank our contacts at the overseas fertilizer plants and institutes which supplied all the samples to our laboratory for analysis: Prof. Chen Jing Yu of the Shanghai Research Institute of Chemical Industry, Shanghai, People’s Republic of China; Mr. Hendro Yuwono and Mr. Y. Rus Isdiyatna of PT Petrokimia Gresik in Gresik, Indonesia; Mr. B.S. Vora of the Gujarat State Fertilizer Company Ltd. in Vadodara, India; and Prof. Selim F. Estefan of the National Research Center in Cairo, Egypt. We thank Gordon Nifong and Michael Lloyd of the Florida Institute of Phosphate Research (FIPR) for their helpful reviews and assistance in locating information on the economics of ammonium sulfate. Financial support for this study was provided by a grant from FIPR (#93-05-040R).

## REFERENCES

- Anonymous, 1994. Ammonium sulfate-prices show growing appeal. *Sulfur*, 234, 28-33.
- Burnett, W.C., 1988. Release of radium and other decay-series isotopes from Florida phosphate rock. Florida Institute of Phosphate Research Report No. 05-016-059, 164 p.
- Burnett, W.C. and W.-C. Tai, 1992. Determination of radium in natural waters by alpha liquid scintillation *Analytical Chemistry*, 64, 1691-1697.
- Burnett, W. C., C. D. Hull, J. E. Young, and P. H. Cable. 1993. A simple self-absorption correction for gamma-ray counting of soils and sediments. 39th Annual Conference on Bioassay, Analytical, and Environmental Radiochemistry, Colorado Springs, CO, October 11 - 15, 1993.
- Butler, M.F., 1969. Ammonium sulfate -- process sales brief. MFB/LO, Ext. 507, 9010/1999, 36p.
- Cutshall, N. H., I. L. Larsen, and C. R. Olsen. 1983. Direct analysis of  $^{210}\text{Pb}$  in sediment samples: self-absorption corrections. *Nuclear Instruments and Methods* 206: 309-312.
- Chen, Jing-Yu, 1990. The trial production results from demonstration plant for production of ammonium sulfate from phosphogypsum. *Phosphogypsum Conference Proceedings*, Orlando, 41-57.
- Ellwood, P., 1968. Sulfate recycle method unites two processes to make nitrophosphate. *Chemical Engineering*, Feb. 26, 1968, 124-126.
- FAO/UNIDO/World Bank, 1983. Current World Fertilizer Situation and Outlook, 1981/82-1987/88. FAO/UNIDO/World Bank Working Group, Food and Agricultural Organization of the United Nations (FAO), Rome, Italy.
- Gopinath, N.D., 1968. Disposal or use of gypsum in production of ammonium sulfate. In: Phosphoric Acid, v. 1, Part II, (ed. A.V. Slack), Marcel Dekker, New York, 541-566.
- Kanwar, J.S. and M.S. Mudahar, 1986. Fertilizer Sulfur and Food Production. Martinus Nijhoff/Dr W. Junk Publishers, Kluwer Academic Publishers Group, Dordrecht, 247 p.

- Kasturirangan, S.V.N., 1968. Manufacture of ammonium sulfate utilizing by-product gypsum from a phosphoric acid plant. Proceedings Fertilizer Production, Technology and Use, Kiev, Ukrainian Soviet Socialist Republic, August 25 - Sept. 11, 1965, United Nations, New York, 204-209.
- Kouloheris, A.P., 1980. Chemical nature of phosphogypsum as produced by various wet process phosphoric acid processes. In: Proceedings of the International Symposium on Phosphogypsum, Lake Buena Vista, Florida (eds. D.P. Borris and P.W. Boody), Florida Institute of Phosphate Research, 8-35.
- Lindeken, C.L., 1980. Radiological considerations of phosphogypsum utilization in agriculture. In: Proceedings of the International Symposium on Phosphogypsum, Lake Buena Vista, Florida (eds. D.P. Borris and P.W. Boody), Florida Institute of Phosphate Research, 459-480.
- Lindeken, C.L. and D.G. Coles, 1978. The radium-226 content of agricultural gypsums. In: Radioactivity in Consumer Products (eds. A. Moghissi, P. Paras, M. Carter, and R. Barker), U.S. Regulatory Commission Report No. NUREG/CP-0001, 369-375.
- Miller, R.L. and H. Sutcliffe, 1984. Effects of three phosphate industrial sites on ground-water quality in Central Florida, 1979-1980. U.S. Geological Survey Water Resources Investigations Report 83-4256, 184 p.
- Ramachandran, K.S., K.C. Geevarghese, K. Sasi, and A.P. Rao, 1992. Utilisation of phosphogypsum and work done at FACT. Fertiliser News, 37: 27-30.
- Recheigl, J.E., 1991. Sulfur fertilization improves bahiagrass pastures. Better Crops with Plant Food, Potash & Phosphate Institute, Atlanta.
- Recheigl, J.E., 1992a. Use of by-product phosphogypsum to correct sulfur deficiencies in forage. Proceedings of the 42nd Annual Meeting Fertilizer Industry Round Table, Baltimore, 133-138.
- Recheigl, J.E., 1992b. Sulfur fertilization of bahiagrass forage. Agriculture, 16, 39-42.
- Roessler, C.E., 1984. The radiological aspects of phosphogypsum. In: Proceedings of the Seminar on Phosphogypsum, Miami, Florida Institute of Phosphate Research, 11-36.

- Roessler, C.E., 1988. Radiological assessment of the application of phosphogypsum to agricultural land. In: Proceedings of the Second International Symposium on Phosphogypsum, (ed. G.M. Lloyd), Miami, Florida; Florida Institute of Phosphate Research, 5-23.
- Sacher, E., 1968. Ammonium sulfate from phosphogypsum. Proceedings from the I.S.M.A. Technical Conference, Brussels, Sept. 10-13, 1968, ISMA-68-654, 1-13.
- Schultz, J. J., 1992: An examination of the environmental issues facing the phosphate fertilizer production sector - indicated cost of environmental compliance. Phosphate Fertilizers and the Environment, Tampa, FL, (ed. by J.J. Schultz). 283-309.
- Sill, C.W. and D.G. Olson, 1970. Sources and prevention of recoil contamination of solid-state alpha detectors. Anal. Chem. 42: 1596-1607.