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MICROBIOLOGY AND RADIOCHEMISTRY OF PHOSPHOGYPSUM

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MICROBIOLOGY AND RADIOCHEMISTRY OF PHOSPHOGYPSUM

FINAL REPORT

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PERSPECTIVE

Gordon D. Nifong, Ph. D.

Florida Institute of Phosphate Research

Since its inception more than fifteen years ago, the Florida Institute of Phosphate Research has stressed research in the environmental aspects of phosphate mining and processing. Included in that emphasis has been the health and safety of industry employees and also the public that live in the vicinity of the industry or who are otherwise affected by its operations. The legislation that created the Institute empowered it in a first directive to conduct or sponsor environmental studies as may be necessary for the health, safety, and welfare of Florida's citizens, especially those in the phosphate region. This directive has been heeded closely in the Institute's mission, as most recently described in the 1995 publication "Strategic Initiatives and Applied Research Priorities." It is recognized that protection of the public health and of the environment are implicit goals of all Institute research, but also there are areas of special interest, including air and water pollution, natural radiation, indoor radon, land reclamation, and the handling and storage (and possible use) of by-product phosphogypsum. Although these areas overlap somewhat, it is the gypsum issue that this current project most directly addresses.

Naturally occurring radioactive materials are ubiquitous over all the earth, but are elevated above background in phosphate minerals. Chemically processing phosphate rock into phosphoric acid and phosphogypsum partitions the radionuclides present in the ore in such a way that most radium, and hence its decay products radon, polonium and lead, remain with the gypsum, while uranium and thorium remain with the acid. Largely because of this elevated level of natural radioactivity, little use for phosphogypsum has been found, and indeed the U. S. Environmental Protection Agency currently bans most use and instead requires the material to be left in storage at the plant site. About 700 million tons are currently stockpiled in Florida. Thus over the years the Institute has funded much phosphogypsum research, including the effects of leaving it in storage, and the effects of using it in agriculture, in construction, and in the recovery of sulfur. More recently the risks to health and the environment of using phosphogypsum versus the risks of storing it have been emphasized, along with technical and economic considerations of each alternative.

This study by investigators at Florida State University addresses the gypsum issue in four ways. A first topic is an expanded characterization of radionuclides present in the material. Part two explores the actual sites in the gypsum where the nuclides are concentrated, a first step in any purification process. A third section examines the impact on near-by groundwater of phosphogypsum storage. Finally any relation between the nuclides, mainly polonium, and certain bacteria, mainly those involved in sulfur cycling, was explored for any potential of using bacteria to release radionuclides from the gypsum or to remove them from process waters.

MICROBIOLOGY AND RADIOCHEMISTRY OF PHOSPHOGYPSUM

EXECUTIVE SUMMARY

Phosphogypsum, a waste by-product derived from the wet process production of phosphoric acid, represents one of the most serious problems facing the phosphate industry today. This by-product gypsum precipitates during the reaction of sulfuric acid with phosphate rock and is stored at a rate of about 30 million tons per year on several stacks in central and northern Florida. The main problem associated with this material concerns the relatively high levels of natural uranium-series radionuclides and other impurities which could impact the environment and which makes its commercial use impossible. Our general approach to this problem was to start the task of detailing exactly where and how radionuclides are hosted within the material. In this way, it is hoped that ultimately one may develop purification schemes for this waste material.

Our experimental approaches for characterizing the radiochemistry and microbiology of Florida phosphogypsum has been directed along four specific lines of research. One component of this study involved detailed analyses of the same radionuclides in the phosphate ore rocks and the phosphogypsum. Another component includes preliminary investigations of radionuclides in shallow groundwaters collected from a limited number of monitor wells adjacent to gypsum stacks. The majority of research in the third component of this study involves dissolution and leaching studies of the phosphogypsum and developing techniques to isolate and concentrate specific radionuclides from the phosphogypsum matrix. The ultimate goal of this line of research was to identify the actual sites occupied by individual nuclides and how they are bound in the phosphogypsum. The final research component concerned microbiological studies which endeavored to identify and culture bacteria that either show the ability to release radionuclides from phosphogypsum or have promise of scavenging radionuclides from fluids that are associated with the material. The microbiological research was focused on microbes which metabolize Po and may play a role in the solubility and mobility of Po (and perhaps other radionuclides) in solutions circulating in and through gypsum stacks.

This Final Report presents data and discussion of these efforts which have been made since the study was initiated in 1992. The report is organized to show how these

research topics were addressed: **Chapter 1** presents general radiological data for phosphate ore rock, phosphogypsum that has been stored on gypsum stacks for various times, and water samples from monitor wells adjacent to phosphogypsum storage areas in Florida. The primary objective of the research described in this chapter was to radiochemically characterize and provide a comprehensive data base of uranium-series nuclides in Florida phosphogypsum and ore rocks. By evaluating all significant nuclides, including ^{226}Ra, ^{210}Pb, and ^{210}Po in pairs of ore rock feed materials and phosphogypsum , sufficient data were obtained to describe fractionations between the various members of the ^{238}U decay chain during processing. A thorough sampling of phosphogypsum of various ages stored in Florida has also been completed in order to assess whether some radioelements migrate preferentially to others during storage.

The actual location of uranium-series radionuclides within phosphogypsum was investigated in more detail in **Chapter 2** by several different approaches. The hope here was that if the actual sites within the phosphogypsum that host radionuclides could be identified, this may represent a first step towards radiochemical purification of this material. In this way, a waste material that may potentially contaminate the environment could ultimately be put to some good use. The material presented in Chapter 2 is an extension of the broad-based radiochemical research presented in Chapter 1. We describe methods that have been investigated for fractionating, concentrating, and leaching radionuclides from Florida phosphogypsum by both physical and chemical methods. Our results show that the behavior of radium, and other radionuclides, is often sample dependent, i.e., there are significant differences in the solubility of radionuclides for different samples. In general, about 10-50% of the radium in Florida phosphogypsum is water soluble, although there are some data which suggest that the radium is actually associated with extremely fine-grain particles, perhaps colloids. The remaining, water-insoluble radionuclides are associated with the major elements Al, Fe, and P and the minor elements Ba, Sr, and rare-earth elements (as Ce and La). Our data suggest that the radionuclides appear to be hosted in an aluminum-rich phase, probably an aluminum phosphate resembling the mineral crandallite. The ultimate controls which govern the observed differences between phosphogypsurn samples still eludes us although substantial progress has been made in detailing the mechanisms which influence release and migration of radionuclides from phosphogypsum.

Chapter 3 concerns investigations related to the elevated concentrations of ^{210}Po, the last radioactive member of the ^{238}U decay-series, which have been reported in a number of shallow wells from the Central Florida Phosphate District. Although the exact source is uncertain, the ^{210}Po probably originates either from the naturally-occurring phosphate rock of the area or from phosphogypsum. We assessed the potential of a bacterial isolate to remove and incorporate dissolved polonium from solution by conducting comparative radiotracer experiments using $^{35}SO_4$ and ^{208}Po. Since the observed chemical concentration of Po in these wells is too low to serve in any direct metabolic function, it was suspected that it might be cometabolized with its chemical analog sulfur. Our experiments were designed to (1) measure the rate of isotope uptake as a function of bacterial growth; and (2) fractionate the bacteria into various cellular components to determine how polonium and sulfur were partitioned within the cell. Results indicated that while the initial uptake mechanisms for SO_4 and Po differ, once associated with the bacterial cells, polonium is dispersed between the cell walls, cytoplasm, and protein in a manner similar to sulfur. The uptake rate of polonium is sufficiently rapid that the potential exists for development of a bioremediation scheme for removal of polonium (and perhaps other contaminating ions) from process waters and other aqueous solutions.

The research reported in Chapter 4 is an extension of the uptake experiments presented in the previous chapter. In this section, we investigated the more environmentally significant bacterial release of polonium from phosphogypsum. Because of the chemical similarity of Po to sulfur (both occupy the same column in the periodic table) studies were initiated to determine whether bacteria, particularly those species active in sulfur cycling, could account for the selective solubilization and mobilization of Po. This chapter reports on experiments involving interaction of bacteria with this waste gypsum. Bacteria were isolated from gypsum that were capable of mediating Po release in column experiments when fed a growth medium. Sulfate-reducing bacteria were particularly effective at mediating Po release provided the sulfide levels did not rise above 10 µM, in which case Po was apparently co-precipitated as a metal sulfide. Thus, whether microbes release or take up polonium in this system depends upon the prevailing environment (oxic or reducing) which will ultimately dictate which bacteria are present.

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CHAPTER 1

RADIOCHEMISTRY OF PHOSPHOGYPSUM

INTRODUCTION

The majority of the phosphate fertilizer industry in North America is located in Florida, which contains one of the world's largest deposits of natural phosphorite. In the late 1970s, Florida supplied over 80% of the national output and more than 30% of world production of phosphate ore. As in most other phosphate deposits, the Florida ores contain from about 50 to 500 parts per million (ppm) uranium. Sweeney and Windham (1979) estimated the Central and South Florida Phosphate districts contain 3.7 x 10^5 metric tons of U_3O_8. Deposits of sedimentary phosphorites in northeastern Florida which contain less uranium are also exploited for phosphate. The daughters of ^{238}U, usually in radioactive equilibrium within the phosphate rock, are fractionated during reaction of the phosphate rock with sulfuric acid during the production of phosphoric acid. The solid by-products and the processing fluids used in the manufacturing process have the potential to be radiologically, as well as chemically, damaging to the environment.

Although phosphoric acid can be made in a variety of ways, the most common method is the so-called "wet-process" production in which phosphate rock is reacted with sulfuric acid. Operating conditions in the reaction chamber determine whether gypsum is crystallized in either the dihydrate ($CaSO_4 \cdot 2H_2O$) or hemihydrate ($CaSO_4 \cdot 1/2H_2O$) form. The capacity of existing phosphoric acid plants is so large that the phosphate fertilizer industry is the largest consumer of sulfuric acid in the world. The process also results in the production of substantial quantities of by-product gypsum known as "phosphogypsum." A very simplified chemical reaction for the dihydrate process may be shown as follows:

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 20H_2O \rightarrow 10CaSO_4 \cdot 2H_2O + 6H_3PO_4 + 2HF$$

{phosphate rock} {phosphogypsum}

While the mole ratio between gypsum and phosphoric acid is 5:3, the mass ratio is closer to 2.9:1, *i.e.,* almost 3 tons of gypsum are produced for every ton of phosphoric acid. The mass ratio of phosphogypsum produced to phosphate ore rock reacted is about 1.7:1 based on this equation, but is probably less and varies with the proportion of sand and unreacted solids in the ore rock. As a consequence of this approach, the phosphate industry as it operates in most parts of the world could more accurately be termed a gypsum industry. Since the phosphate industry measures its phosphoric acid production in terms of many millions of metric tons per year, the amount of by-product gypsum produced is clearly substantial, currently on the order of 100 million tons per year on a worldwide basis.

The solid by-products, predominately phosphogypsum with lesser quantities of quartz sand, clays, and minor unreacted phosphate ore are mixed with processing/cooling water solutions and pumped as a slurry with approximately 20% solids to storage areas, the so-called gyp-stacks. The slurries are discharged on the top of stacks and processing solutions drain through the pile of by-product. Solutions discharge through the base of the older stacks which are not lined and large containment channels along stack perimeters collect discharging solutions which have low pH and high concentrations of SO_4, F, Na, Ca, some trace metals and radionuclides. These solutions are then ponded and re-used in the production process.

According to a review by Nifong (1988) , the principal environmental concerns with phosphogypsum storage are fluorine emissions to the atmosphere and possible contamination of groundwater with radium, sulfate, and fluoride due to leaching of the phosphogypsum stack by processing solutions or rain water. The problem associated with phosphogypsum storage that is perceived as being of greatest concern, at least in the United States, is its content of radioactive elements, especially ^{226}Ra **(Fig 1).** Other uranium-series nuclides associated with phosphogypsum, including ^{210}Po, have been found at high concentrations in some shallow groundwaters in the Florida mining area (Harada *et al.*, 1989; Upchurch *et al.*, 1991) and may be related to phosphogypsum in some cases. Generally the concern is focused on the potential impact on the environment in the immediate vicinity of the gypsum stacks (Kouloheris, 1980; Miller and Sutcliffe, 1984).

Although phosphogypsum has been used in Japan and some other 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. The U.S. Environmental Protection Agency (USEPA) has ruled that gypsum must be placed on stacks or in mine cuts and only limited quantities can be removed for agricultural (^{226}Ra<10pCi/g) or research purposes. Phosphogypsum cannot be used for construction or similar applications in the United States following an EPA

ruling (57 Fed Reg 23305, June 3, 1992) and reconsideration of this ruling (57 Fed Reg 14040, March 24, 1994). This ruling was predicated on: (1) risk assessments and environmental concerns associated with radionuclides in the ^{238}U decay chain, especially radon; and (2) the substantial amount of natural gypsum already produced in the U. S. This situation is unfortunate for Florida, where the inventory of by-product gypsum has been growing tremendously within the past few decades. This problem does not exist in some countries. For example, at this time the UK and the Netherlands discharge phosphogypsum into rivers or the sea, Morocco plans to pump 25,000 tons/day of phosphogypsum from one plant directly into the Atlantic Ocean, and France until recently discharged into the mouth of the Seine River (Becker, 1989; McDonald *et al.*, 1992; Germain *et al.*, 1992; Köster *et al.*, 1992; Pennders, *et al.*, 1992).

Although no industrial discharge of phosphogypsum into the environment continues today in the United States, there was a plant near Taft, Louisiana that discharged a substantial amount of phosphogypsum directly into the Mississippi River from the 1960's to the mid-1980's (Kraemer and Curwick, 1990). It may be fortunate that this discharge has been stopped. A radiological assessment by McDonald *et al.* (1992) of the dose received by the public in the UK has shown that there is actually a higher potential exposure from eating seafood near the Whitehaven phosphogypsum outfall than from the nearby Sellafield operations which have had significant discharges from a plutonium reprocessing facility. Nevertheless, stockpiling has its own problems because of the tremendous volumes that are produced. In Florida, it is estimated that more than 700 million metric tons of phosphogypsum are already stored at 18 sites throughout the state, with 30 - 40 million tons being added each year. At this pace, Florida will have nearly 1 billion ($1x10^9$) metric tons of stockpiled phosphogypsum by the year 2000 (May and Sweeney, 1982; Nifong, 1988).

Phosphate Ore Rocks and Phosphoric Acid Production

On a world-wide basis, the total production of phosphate rock has averaged between 150-160 million tons per year from 1987 to 1991 (E&MJ, 1993). Because fertilizer manufacture accounts for the overwhelming majority (>95%) of this production, the long-term growth will ultimately be driven by human population growth which is expected to continue to increase for at least several more years (Brown et al., 1987). Phosphate ore rocks are widely distributed in Florida, but have varying concentrations of phosphate and ^{238}U series radionuclides (Menzel, 1968; Bosch, *et al.*, 1976; Burnett, 1988). Sedimentary phosphorites of most ages and areas (but with some notable exceptions) contain significant uranium concentrations with typical values over 100 ppm. High grade ores in the Bone Valley Formation of the Hawthorne Group in central Florida are predominantly granular to pebble-sized grains of carbonate fluorapatite in a matrix of quartz sand, clays, and organic material. Ore bodies are often weathered and the mineralogy, chemical composition, and distributions of ^{238}U decay series radionuclides in weathered

profiles are complex (Altschuler *et al.*, 1958; Riggs, 1979; Burnett, 1988). Daughter nuclides in the ^{238}U series have been demonstrated to be fractionated during such natural weathering of the ore-bodies, but in phosphorites, as in most naturally-occurring rocks and minerals, radionuclides in the ^{238}U decay-series **(Figure 1-1),** at least as far as ^{226}Ra, are in approximate radioactive equilibrium. One notable exception to this is loss of ^{222}Rn, an inert gas. In an earlier study conducted by our group for the Florida Institute of Phosphate Research (FIPR), we showed that most phosphate rocks in Florida lose between 10-20% of their natural ^{222}Rn content (Burnett, 1988).

Approximately 70% of phosphate ore mined in Florida is initially converted to phosphoric acid before production of soluble phosphatic fertilizers. The granular ore rocks are concentrated or "beneficiated" by removing matrix materials by sizing techniques and flotation in fatty acids. Several studies have shown that after the granular phosphate ore has passed through the beneficiation process, the equilibrium conditions in the uranium decay chain are largely unchanged. Since virtually all economic deposits of phosphorite are old enough for radioactive equilibrium to be established in the ^{238}U decay chain (this requires approximately 1 million years), the specific activity (number of radioactive disintegrations per unit time per unit mass, i.e., decays per minute per gram) of all uranium decay products will be approximately equal. Thus, a Miocene phosphorite in Florida with a uranium content of 100 ppm will not only have a ^{238}U activity of approximately 74 decays per minute per gram (dpm/g), but individual activities of ^{230}Th, ^{226}Ra, ^{222}Rn, etc. of an equivalent amount.

During mining, but especially during chemical processing of the ore, these radioelements become separated and radioactive equilibrium is no longer the case. This creates an entirely different situation because each isolated daughter will behave according to its own chemistry and, if truly isolated, will decay away with its own half-life. For example, should ^{210}Po be released into the environment without its radioactive predecessors, it will decay away with its own half-life (138.4 days), rather than be controlled by longer-lived parents. The radioactive daughters below ^{226}Ra in the chain are often observed to have lower activities due to ^{222}Rn loss. However, during chemical operations such as wet process phosphoric acid production, the radioactive equilibrium in the phosphate rock is disrupted, a redistribution of radioactivity occurs, and the various members of the decay series follow separate pathways as determined by their chemical properties.

Composition of Phosphogypsum

The chemical and radiochemical composition of phosphogypsum depends upon the composition of the phosphate rock used for feed material and on the acid processing method employed. While three methods of processing are currently used throughout the world, only two are in use in Florida, the dihydrate process

Radionuclides in Phosphogypsum

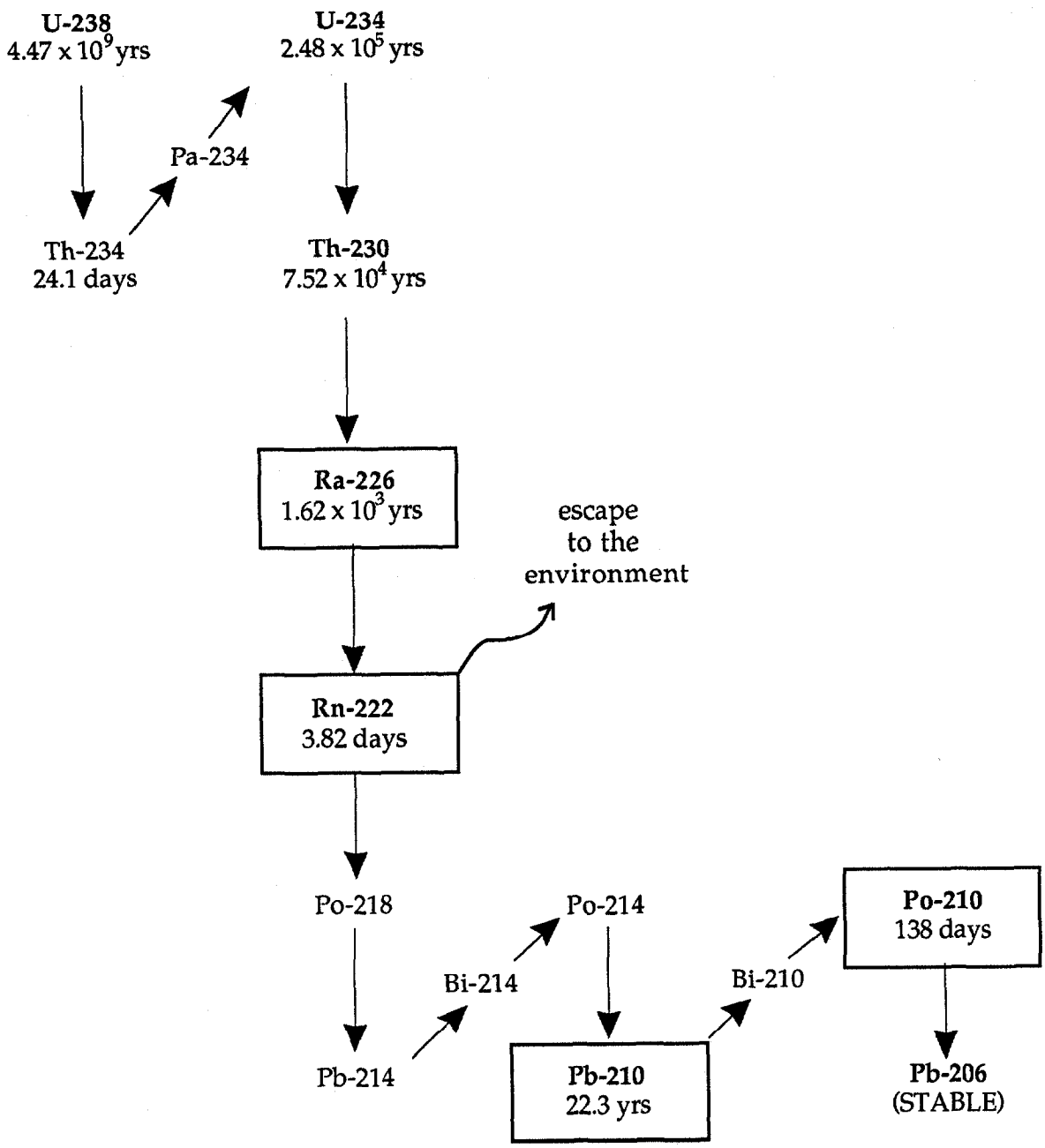

Fig. 1-1 Natural ^{238}U decay chain with nuclides of interest to this study enclosed in boxes. Downward arrows indicate alpha particle decay and diagonal arrows represent beta decay.

used throughout the Central Florida Mining District and the hemihydrate process used in northern Florida. Typical chemical compositions of two hydrated forms of phosphogypsum from these processes are given in **Table 1.** Detailed chemical compositions and some radioisotopic analyses of phosphogypsum have been published (Ferguson, 1985; Becker, 1989; Luther, 1991; McDonald *et al.*, 1992; Germain *et al.*, 1992; Köster *et al.*, 1992; Pennders, *et al.*, 1992; Luther and Dudas, 1993; Luther *et al.*, 1993; Rutherford *et al.*, (1993, 1994, submitted), Arocena *et al.*, (submitted). The Dudas research group at the University of Alberta has an extensive database of phosphogypsum compositions. The most recent detailed compositional analyses for Florida phosphogypsum have been reported by Carter and Scheiner (1992). Typical examples of these compositions are given in **Table 2.** In terms of the radioisotopic composition, phosphogypsum contains the same radionuclides, but in distinctly different ratios than its phosphate rock raw material. These radioisotopic differences are discussed at length in a later section.

Previous Work

Even though a considerable amount of compositional data exist for phosphogypsum produced throughout the world, comparatively little detailed work had been undertaken on the fractionation and re-distribution of ^{238}U decay-series radionuclides during processing of the ores and during storage on stacks. Radionuclide data, when presented, are generally confined to analyses of U, Th, and Ra. Rutherford *et al.*, (in press) have recently given some analyses of ^{210}Pb in phosphogypsum, but the most complete published analyses for ^{238}U decay chain isotopes that we have been able to locate are those published by Horton *et al.*, (1988). Our studies focus on Florida ores and by-products and only a very few radiochemical studies of Florida phosphogypsum that were conducted prior to 1990 contain data on the activities of several radionuclides in the uranium decay-chain. Most previous radiochemical studies of phosphogypsum up to that time usually presented data for gross alpha activities and / or ^{226}Ra.

Studies by Guimond and Windham (1975), Lardinoye *et al.*, 1982; Roessler (1984, 1988), May and Sweeney (1982), Laiche and Scott (1991); Burnett *et al.*, (1992), and others have consistently shown that uranium tends to follow the phosphoric acid phase, while most of the radium is incorporated into the phosphogypsum. A very limited number of analyses (Guimond and Windham, 1975; Roessler, 1984) present data that implies thorium tends to follow the phosphoric acid phase. Even higher activities of ^{226}Ra (up to 220,000 dpm / g) are found in the small quantities of scale associated with the filter pan which separates gypsum from the phosphoric acid (Keaton, 1987; Burnett *et al.*, 1993). The French scientist J. Moisset has attempted to locate radium site(s) in phosphogypsum as an integral part of an approach to find a way to radiochemically purify phosphogypsum. He proposed that radium is probably located together with calcium, strontium, and barium sulfate in small crystals of 4-8 µm in diameter (Moisset, 1988). Another population of even smaller (about 1 µm diameter) crystals of unidentified composition were also

Table 1. Typical analyses of phosphogypsum (from Kouloheris, 1980).

Component	Dihydrate process	Hemihydrate process
CaO	32.5	36.9
SO_3	44.0	50.3
P_2O_5	0.7	1.5
F	1.2	0.8
SiO_2	0.5	0.7
Fe_2O_3	0.1	0.1
Al_2O_3	0.1	0.3
MgO	0.1	-
H_2O	19.0	9.0
Total	98.2	99.6

Table 2. Detailed compositional analyses of three Florida phosphogypsum (dihydrate) samples from Carter and Scheiner (1992) and this study. Concentrations are in mg/Kg. Water in the gypsum structure ($CaSO_4 \cdot 2H_20$) makes up 20.9% (209,000 ppm) by mass and is not accounted for in the total of these analyses. Carbon compounds comprise <1% of most bulk phosphogypsum samples. Fe is total Fe. Concentrations of Cd, As, Hg, Sb, Se, V are less than detection limits for these ICP analyses.

Chemical Component	Florida Phosphogypsum Sample		
	Leach Gyp* (USBM)	Gyp DL3 (FSU)	Gyp-46 (FSU)
Na	1700	160	4110
K	<1000	130	1750
Ca	191500	207200	171910
Mg	<100	50	80
Fe	940	1110	830
Al	1300	810	830
Si	90000	83200	76200
Ti	200	470	220
P	2400	2450	2920
Sr	550	603.5	638.7
Ba	32	80	70
Cr	75	3.1	<1.6
Mn	9.2	20	10
Ni	250	<5	5.1
Cu	195	5.5	<4.2
Pb	<100	10.7	16.6
Zr	<100	30.1	6.2
La	<40	105.7	109.2
Ce	-	58.3	<8.4
F	5750	2700	4240
SO_4	350000	466200	480500
Total (Anhydrous)	~645500	~765390	~744450

* Sample contained 14.8% porewater

tentatively identified as containing significant amounts of radium. Recent work by Rutherford et *al.,* submitted) have addressed the mobilization of ^{226}Ra as phosphogypsum is leached with deionized water and the correlation of Ba:Ra in residues and leachates.

There are few actual analyses of polonium in phosphogypsum although what is available (Hurst and Arnold, 1980 and 1982; Horton *et al.*, 1988) suggests that polonium is strongly favored by the gypsum phase. There is disagreement on what fraction ^{210}Pb is associated: reports by SENES Consultants Ltd. (1987), Roessler (1990) and others suggest that ^{210}Pb follows the phosphoric acid fraction while analyses presented in Horton *et al.* (1988) show that ^{210}Pb is contained in the phosphogypsum.

Objectives of this Research

The primary objectives of the research presented in **Chapter 1** are to radiochemically characterize and provide a comprehensive database of uranium-series nuclides in Florida phosphogypsum and the ore rocks from which the gypsum was derived. We intended to produce a sufficient number of analyses of nuclides in the ^{238}U decay chain, including ^{226}Ra, ^{210}Pb, and ^{210}Po in ore-rock feed material - phosphogypsum pairs, to enable a description of the fractionation between these members, of the ^{238}U decay chain during processing of the ores. In addition, a thorough sampling of phosphogypsum of various ages stored in Florida has been completed in order to assess whether some elements migrate preferentially to others in phosphogypsum storage stacks.

RADIOANALYTICAL PROCEDURES

Solid Sample Collection

Phosphogypsum and beneficiated ore rock samples have been collected from 15 of the 18 gypsum storage stacks in Florida and all but one production facility that is currently producing phosphoric acid. Beneficiated ore rocks were collected from the majority of the production facilities. Ore rock slurries were usually sampled since most production operations mix the ore rock with processing/cooling water before feeding it into reaction vessels. Samples of the resulting "fresh gyp" slurries were collected directly from the discharge pipe which carries the by-product material onto the active phosphogypsum stacks. The phosphogypsum slurries may be mixed with processing fluids again after sulfuric acid reaction to maintain proper viscosity for pumping it to the top of the adjacent gyp stack. Tons of fresh gyp can be deposited on a stack during a typical production day. In addition to the "fresh gyp" that was collected directly from the discharge lines on the stack, some samples were drawn from ports on the discharge lines, and from terrace deposits that are rapidly

constructed into channels beneath discharge lines. Ore rock and phosphogypsum pairs were collected for all but one Florida production facility during 1992 and 1993.

Samples of phosphogypsum was also collected at a number of locations on each stack that was sampled (see Appendix A - Sample Descriptions). The objective was to collect samples that had been on the stack for various lengths of time; *e.g.*, from the oldest material near the base of the stack, gyp that was >6 and <10 years old, >2 and <6 years old, *etc.*, up to the fresh gyp that was being discharged at the time. About 5 kg samples of older phosphogypsum were collected from undersaturated zones of stacks with a shovel after the weathered surface layer was removed. The less friable, weathered horizon was sampled in two near-surface profiles of stack surfaces that had been inactive for decades. Samples of a filter screen from a phosphoric acid plant was also collected and analyzed for radionuclides.

Preparation of Solid Samples for Radiochemical Analyses

Calcium sulfate has three crystalline forms: dihydrate ($CaSO_4 \cdot 2H_2O$), hemihydrate ($CaSO_4 \cdot 1/2H_2O$), and anhydrite ($CaSO_4$). Depending on the chemical process used in phosphatic fertilizer production, calcium sulfate may occur as either dihydrate or hemihydrate in phosphogypsum. Conversions between the three phases based on thermodynamic considerations may be shown as follows (Greenwood and Earnshaw, 1989):

$$CaSO_4 \cdot 2H_2O \xrightarrow{150^\circ C} CaSO_4 \cdot 1/2H_2O \xrightarrow{600^\circ C} CaSO_4$$

dihydrate hemihydrate anhydrite

Since water exists in the crystalline structure of phosphogypsum and a free form, consideration must be given to the methodology of drying these samples before analysis. It is difficult to remove completely free water by air drying samples at room temperature because the sample is influenced by humidity. The “fresh” phosphogypsum samples were very difficult to dry and homogenize due to the hydroscopic properties of the processing solutions, particularly sulfuric acid. It was also observed using X-ray diffraction (XRD) procedures that dihydrate can be partly converted into hemihydrate even at relatively low temperatures (~35° C) in a drying oven. Pure dihydrate or hemihydrate is thus not easily obtained in an oven because phase changes between these two forms cannot be perfectly controlled. Since all radiochemical analyses of solid phase material is ultimately based on a gravimetric determination (specific activities), and there exists a potential mass difference of about 15.7% between dihydrate and hemihydrate, analyses of phase mixtures would result in unacceptable and irreproducible artifacts.

Thus, the processing of phosphogypsum samples for measuring specific activities of radionuclides requires special care. All samples for this study were prepared by drying the sample under atmospheric conditions until moisture was

reduced enough to allow a preliminary grinding of 400 - 600 grams of sample to a grain-size of <500 µm (30 mesh). After drying to constant weight in a vacuum dessicator at room temperature, samples were again ground to a grain-size of <250 µm (60 mesh), split with a powder sample splitter, and stored in sealed glass bottles. XRD patterns were then produced for each sample to identify the predominant crystalline phase(s) of $CaSO_4 \cdot nH_2O$ as well as other phases in the phosphogypsum. Almost all the phosphogypsum samples used in this study are from the Central Phosphate District of Florida and are produced using the dihydrate process. Two hemihydrated phosphogypsum samples and one dihydrate/ hemihydrate mixture produced at a plant in northeastern Florida are also included in the radiological database.

Collection and Measurement of Nuclides in Liquids

We sampled shallow groundwater from wells in the immediate proximity of seven phosphogypsum stacks; at Farmland Industries **(Figure 1-2),** the IMC P-21 stack **(Figure 1-3),** Mulberry Phosphates **(Figure 1-4),** CF Industries **(Figure 1-5),** Occidental Chemical **(Figure 1-6),** Cargill Fertilizer **(Figure 1-7),** and Agrico, South Pierce (map unavailable). Either a peristaltic or submersible pump was used in each well that was sampled to collect several liters of shallow groundwater. Wells were pumped for 20 - 40 minutes and water samples collected after temperature, pH, and conductivity measurements stabilized. Samples were fixed in the field for dissolved sulfide measurements. Samples for radiochemical analysis (except radon) were filtered immediately after collection through a 0.45 µm membrane filter, acidified to a pH<2 with HNO_3, and all radio-tracers and carriers were added before returning to the laboratory. Spiked solutions were allowed to equilibrate for at least three days before chemically processing the samples. Samples for ^{222}Rn were collected in triplicate by syringe and injected into pre-measured amounts of a mineral oil based scintillator. Activities of ^{226}Ra were determined by PERALS (Photon Electron Rejecting Alpha Liquid Scintillation) for a selected group of samples, while ^{210}Pb and ^{210}Po were scavenged from the liquid and electrochemically separated (Narita *et al.*, 1991). Po was spontaneously plated on Ag and measured by alpha spectrometry. Pb was deposited on filters as a sulfate, yields calculated, and ^{210}Pb activities measured by low-level proportional counting. Radon was assayed by standard liquid scintillation counting techniques.

Radon Emanation

Most radium activities in groundwater samples were determined by the radon emanation method. Any ^{222}Rn gas initially present was removed by degassing the solution with helium and then the sample was sealed and stored for several days, during which time ^{222}Rn grew towards secular equilibrium with the ^{226}Ra contained in the sample. The sample was then returned to the stripping system where samples were simultaneously de-emanated using high-purity (99.995%) helium at flow rates of approximately 400 mL per minute. Each gas stream was

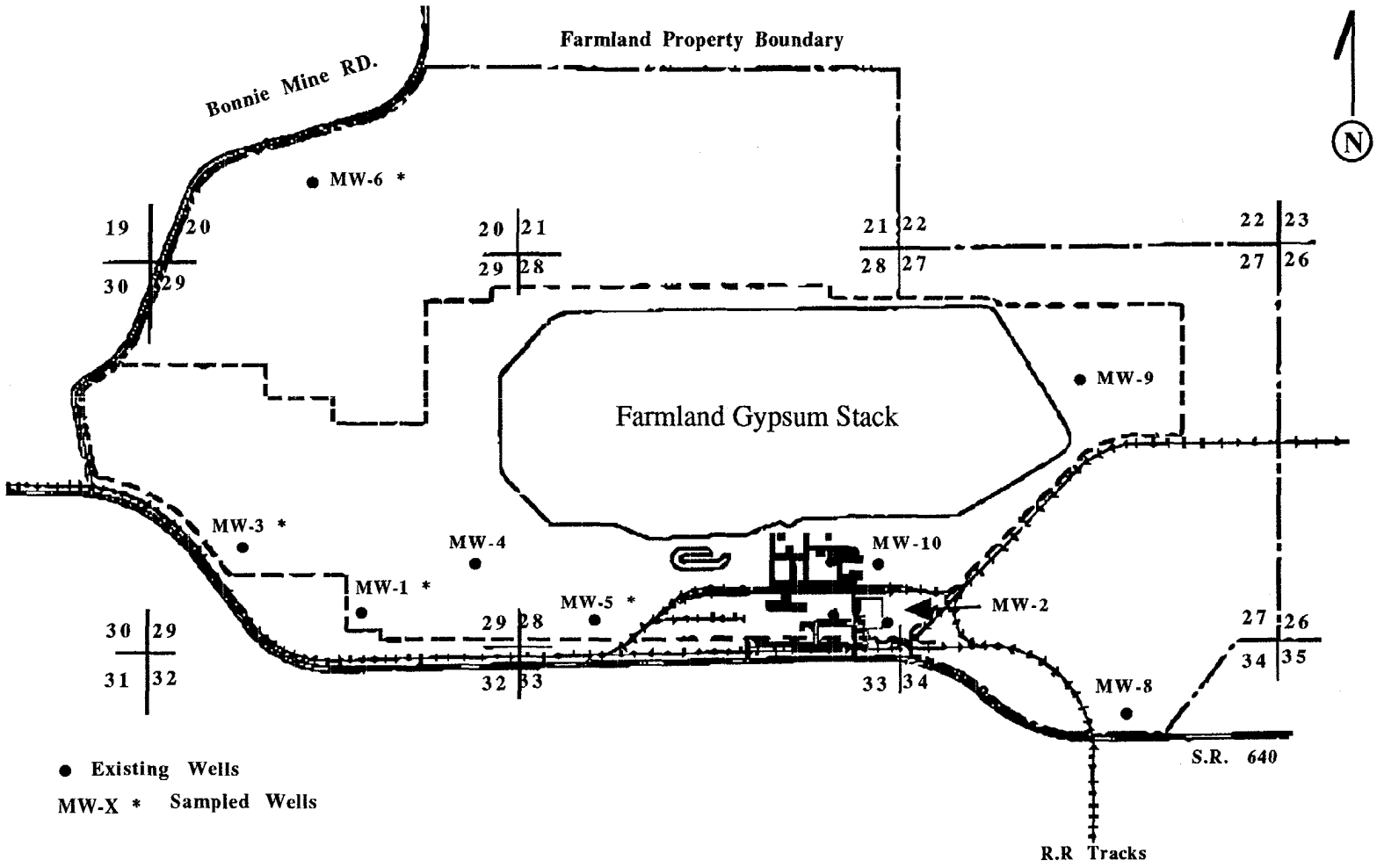

Fig. 1-2 Monitor wells sampled around the phosphogypsum stack at Farmland Industries, Bartow, Florida. Samples were collected from wells 1, 3, 5, and 6.

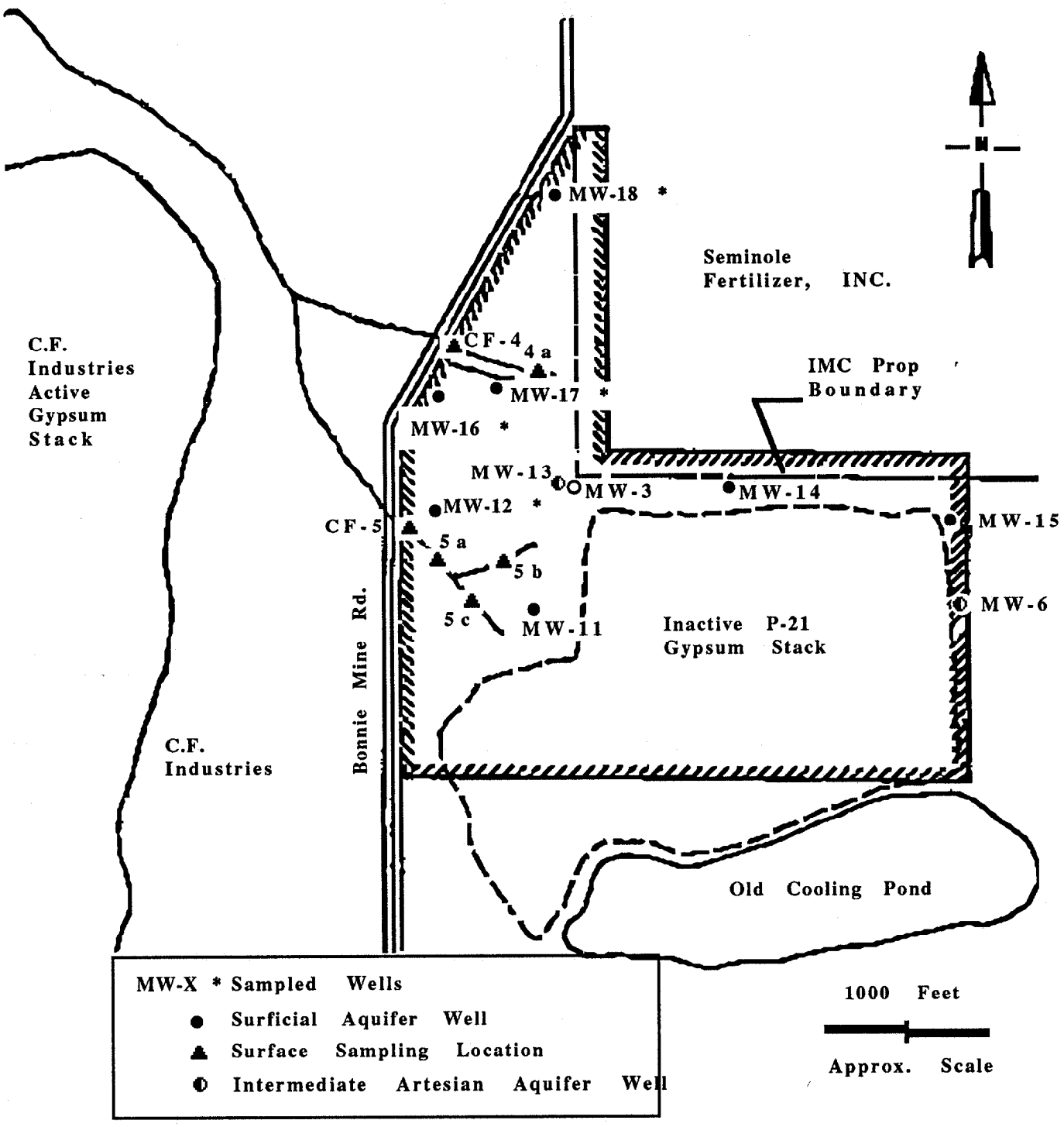

Fig. 1-3 Monitor wells sampled around the IMC P-21 gypsum stack, Bartow, Florida. Samples have been collected from wells 11, 12, 16, 17, and 18.

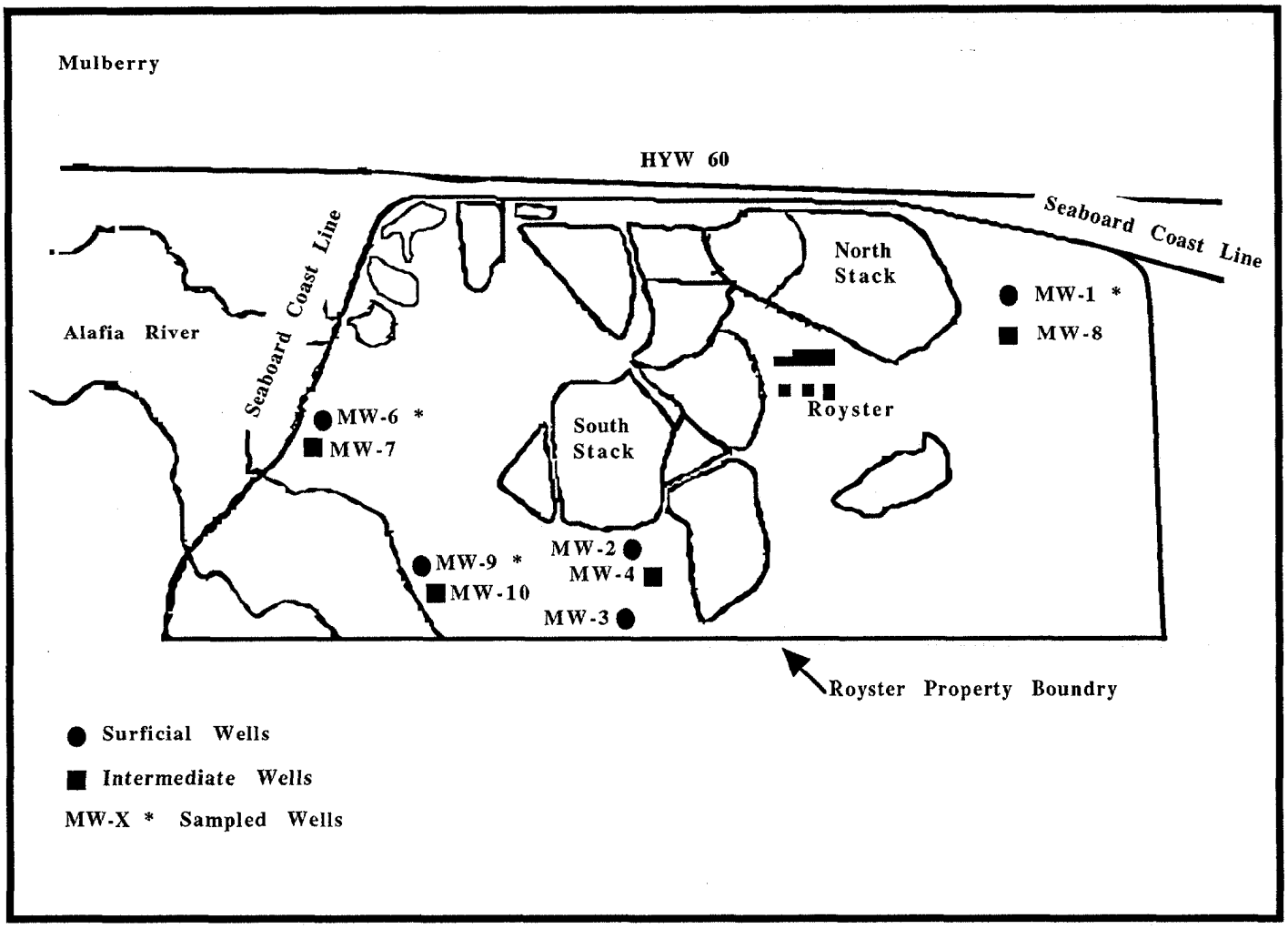

Fig. 1-4 Monitor wells sampled around the gypsum stacks at Royster (now Mulberry) Phosphates, Mulberry, Florida. Samples were collected from wells 1, 6, and 9.

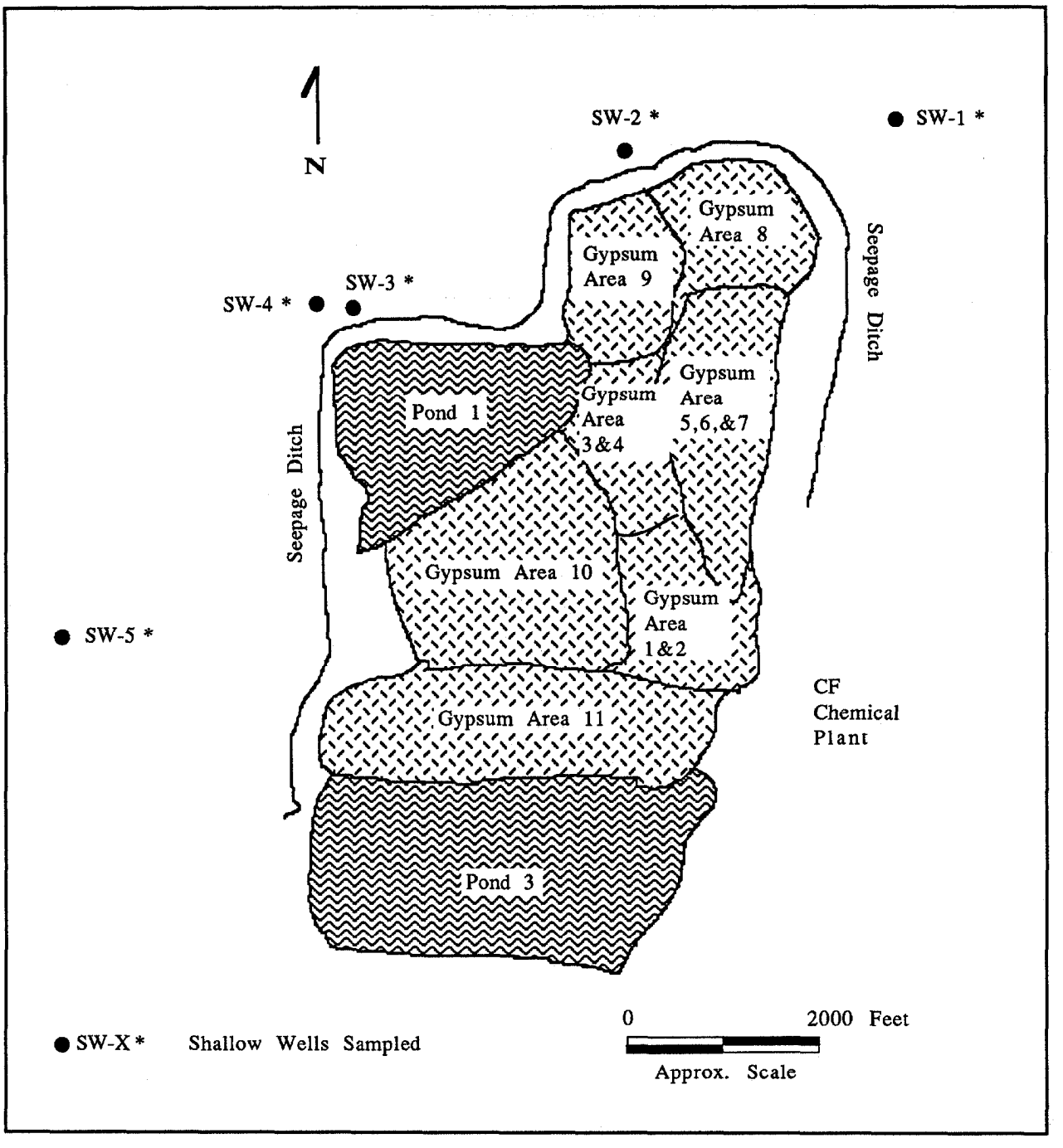

Fig. 1-5 Monitor wells sampled around the gypsum stack at C.F. Industries, Bartow, Florida. Water samples were collected from wells SW-1, 2, 3, and 5.

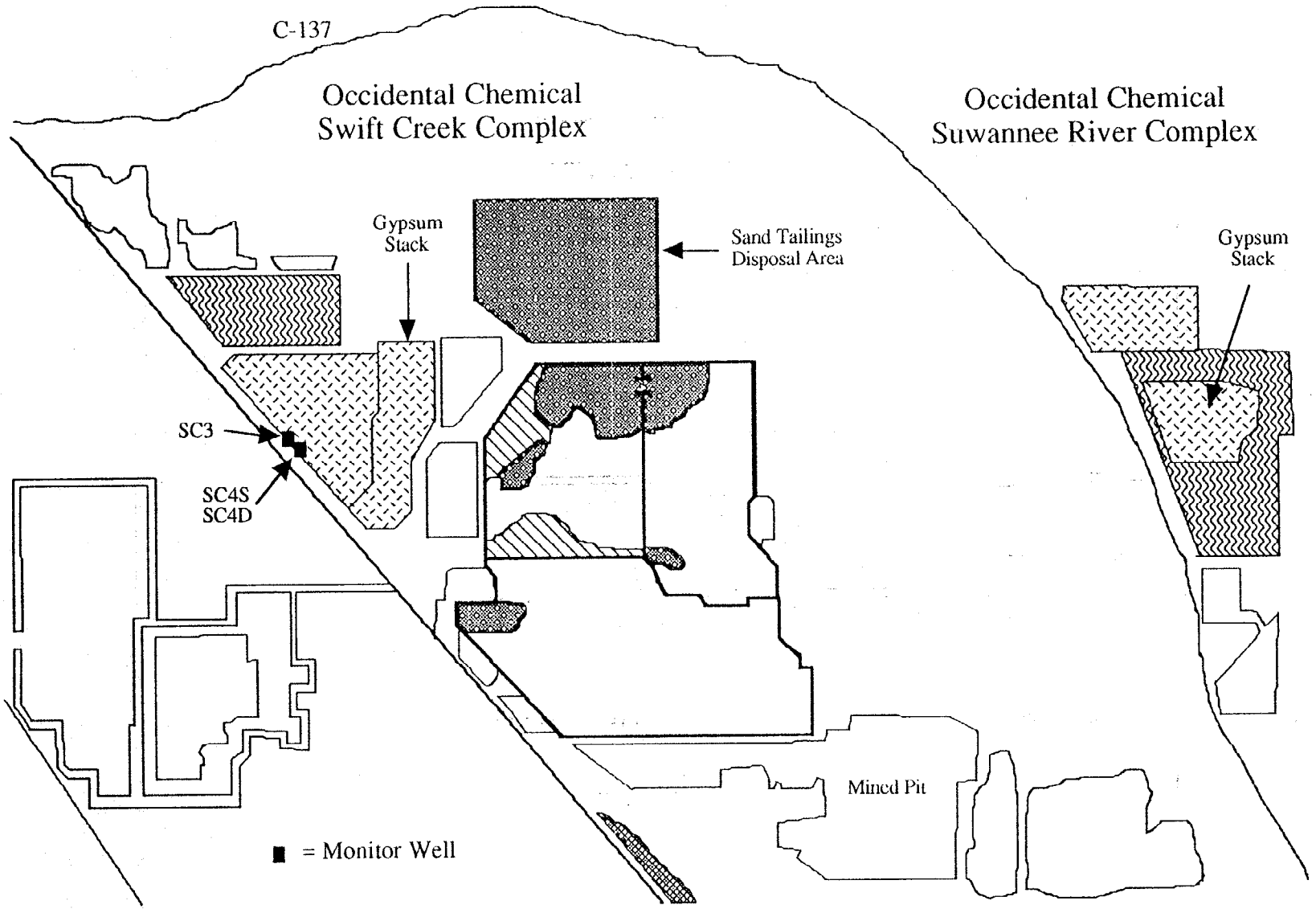

Fig. 1-6 Monitor wells sampled around a gypsum stack at Occidental Chemical, White Springs, Florida. Water samples were collected from wells 3S, 4D, and 4S.

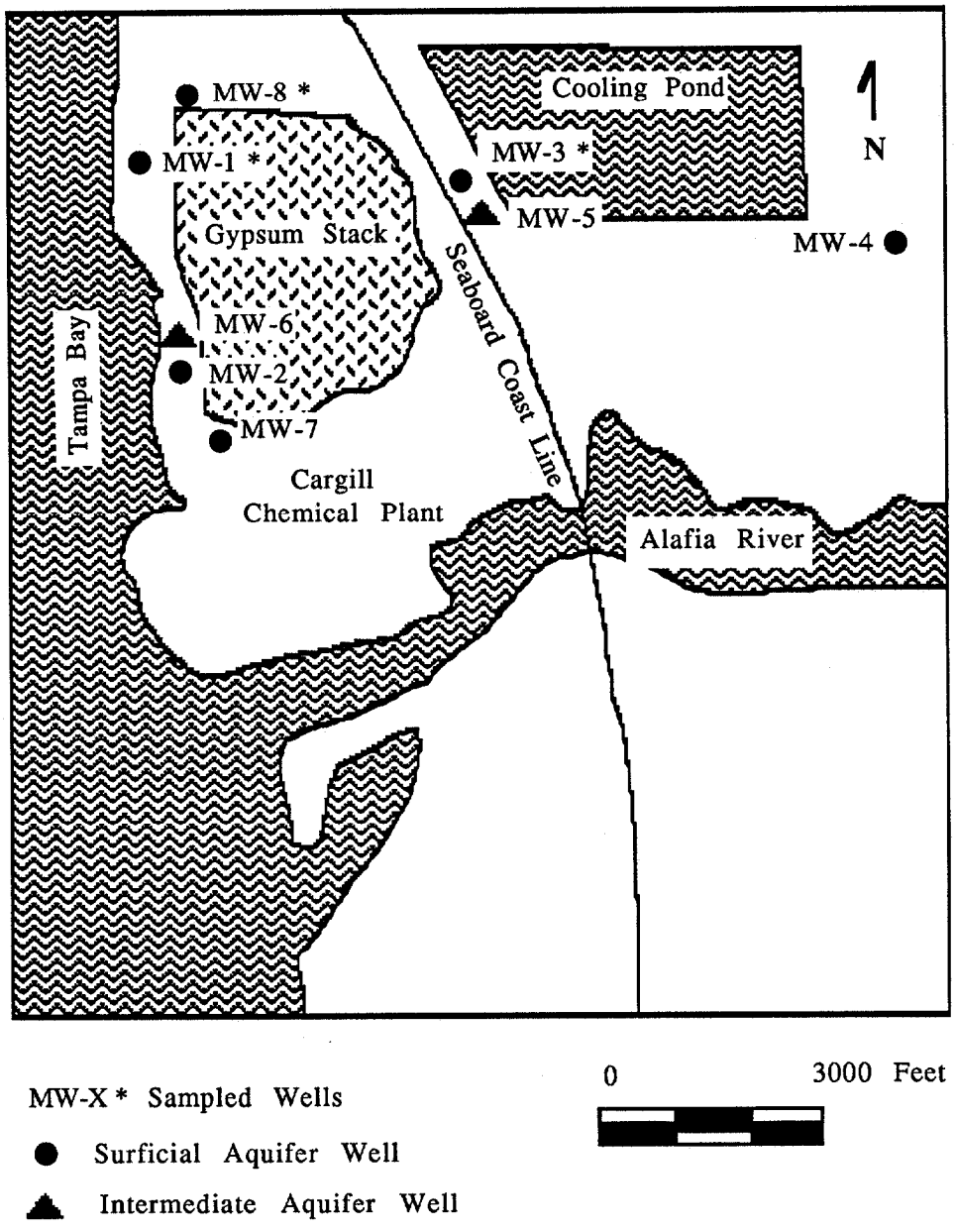

Fig. 1-7 Monitor wells sampled adjacent to a gypsum stack at Cargill Fertilizer, Riverview, Florida. Water samples were collected from wells 1, 3, and 8.

passed through a drying tube filled with Drierite and Ascarite to remove H_2O and CO_2, respectively (Mathieu *et al.*, 1988). The gas streams then flowed into cold traps kept at liquid-nitrogen temperature. Under these conditions, radon will condense in the cold traps while the carrier helium passes through and is ultimately vented to the atmosphere. The length of sample degassing depends upon the sample volume, approximately 50 minutes being suitable for 4-liter samples.

When degassing was complete, the radon was transferred to the alpha scintillation cell by heating the trap with a hot air gun so that the gas "expands" through the cell-fill valve into the evacuated cell. Any radon left in the trap was flushed into the counting cell with helium through the trap (Key *et al.*, 1979). Cells were isolated and removed from the system when the helium pressure reached approximately one atmosphere pressure. After an ingrowth period of approximately 3 hours to establish equilibrium between radon and its immediate daughters, cells were placed on a photomultiplier alpha scintillation counter to count the ^{222}Rn and its a-emitting daughters, ^{218}Po and ^{214}Po (Ivanovich and Harmon, 1982). Activities of ^{226}Ra were then calculated from the equation:

$$A = \frac{R}{3 \times E} \times \frac{1}{(1-e^{-\lambda t_1})} \times \frac{\lambda t_3}{e^{-\lambda t_2}(1-e^{-\lambda t_3})}$$

where:

A = activity of ^{226}Ra (dpm);
R = the net sample count rate;
E = the total system efficiency (includes stripping, trapping, transferring, and cell counting efficiencies) expressed as a fraction (the factor of 3 accounts for the decays due to ^{218}Po and ^{214}Po as well as ^{222}Rn);
λ = the radioactive decay constant of ^{222}Rn (1.253 x 10^{-4} min^{-1});
t_1 = radon ingrowth time, i.e., time measured from the end of the initial degassing period of the sample to the end of the current sample emanation (min);
t_2 = time from the end of sample flushing to the beginning of counting (min); and
t_3 = counting time (min) .

Cell backgrounds were determined prior to processing each sample. Backgrounds of the cells used for this study generally ranged from 0.1 to 0.5 cpm with an average of approximately 0.2 cpm. Helium circulation blanks were run once a month and averaged about 0.5 cpm above background. The system efficiencies were determined by repeated analysis of NIST radium solution standards.

High Precision Gamma-ray Spectrometry

Two intrinsic germanium (IG) detectors with different geometries (one well-type detector manufactured by Canberra and a closed-end coaxial IG detector made by Ortec were used in this investigation to determine ^{234}Th (^{238}U daughter), ^{228}Ac (^{228}Ra daughter), ^{226}Ra, and ^{210}Pb activities in homogenized samples of phosphogypsum. The ^{226}Ra activity was determined by taking the mean activity of three separate photopeaks of daughter nuclides: ^{214}Pb at 295.2 keV and 351.9 keV, and ^{214}Bi at 609.3 keV. Photopeaks of ^{214}Bi at 1120.2 keV and 1764.5 keV were also observed for comparative purposes, but not used in calculating the mean activity of ^{226}Ra by daughter nuclides. The 186.1 keV gamma ray directly associated with the ^{226}Ra alpha decay to ^{222}Rn was not employed because of its lower abundance and interference from the 185.7 keV gamma ray associated with the decay of ^{235}U. However, in the phosphogypsum samples the activity of ^{235}U is so low that this interference is almost negligible, and comparison of the 186.1 keV ^{226}Ra decay gamma with those of the ^{214}Pb and ^{214}Bi photopeaks can serve as a useful check of the radioactive equilibrium between ^{226}Ra and ^{222}Rn in the sample container. Because phosphogypsum does not retain ^{222}Rn well, it is necessary to wait for about 3 weeks to ensure that ^{222}Rn has reached equilibrium with ^{226}Ra before counting since photopeaks due to decay of radon daughters (^{214}Pb and ^{214}Bi) are used to assess ^{226}Ra activities. It is also possible that Th is fractionated from U during processing so "fresh" samples of phosphogypsum and of phosphate ore rocks were reanalyzed after 6 or more months (^{234}Th $t_{1/2}$ of 24.1 days) to assure that ^{234}Th was in radioactive equilibrium with its parent ^{238}U.

Selected samples of dried and ground phosphogypsum, ore rock, and standards were loaded into 10-mm diameter, plastic vials to constant 33 mm height and sealed with epoxy glue to prevent radon escape and measured in the well-type IG detector. Samples and standards for measurement on the coaxial IG detector were dried at room temperature and thoroughly homogenized prior to packing the samples in 100 cm^3 aluminum cans that were then sealed with an aluminum lid lined with a gas impermeable compound. Standards and laboratory secondary standards were counted a number times throughout this study on our well-type IG detector to assure close calibration of energies for each radionuclide analyzed by gamma spectrometry and to maintain high quality analyses. The well detector was calibrated using a series of natural soils, sediments, and rock standards including: NIST 120b (phosphate rock standard); NIST 4353 (Rocky Flats soil); NIST 694 (western phosphate rock); the EPA's Environmental Monitoring Systems Laboratory (EMSL) Pitchblende, Climax Mine tailings, Monazite Ore, and Composite standards; IAEA-306 (sea sediment); IAEA-135 (radionuclides in sediment); and IAEA-152 (powdered milk contaminated with ^{40}K, ^{90}Sr, ^{134}Cs, and ^{137}Cs). Two or more certified activities for each radionuclide in replicate vials of primary standards are used to set well detector efficiencies. Uncertified but "recommended values" for low

activities of ^{238}U decay chain nuclides in IAEA-312 and 314 are also used to monitor well detector efficiencies and MDAs for nuclides on this system. A secondary, interlaboratory standard of sediments from Lake Rowell, Florida which has been analyzed numerous times in four radiochemistry laboratories for ^{238}U decay chain nuclides and two interlaboratory phosphogypsum standards are also used to evaluate efficiencies for each energy used on the well detector.

The coaxial IG detector was calibrated by analysis of the same NIST and IAEA primary standards. Unfortunately, the amounts of EMSL standard samples available to us were not sufficient for packing larger, 100 cm^3 containers for the coaxial detector. In addition to calibrating the coaxial IG detector efficiencies with primary standards, four well-homogenized phosphogypsum samples, two secondary standards, and five primary standards were analyzed on the well detector and larger replicates of these same samples were used to cross check results on the coaxial IG detector. Since some phosphogypsum samples contain up to 11% by mass of sand, clay, and fine-grained aluminophosphates with elevated U activities, it was suspected that heterogeneities in 2 to 3 gram, sub-samples of phosphogypsum measured by γ spectrometry on the well-type IG detector could introduce analytical uncertainties. Therefore, gamma activities in approximately 130 g samples were measured one or more times on the coaxial IG detector for every phosphogypsum and ore rock sample and are reported in the radio-chemical database for this study (the complete database is given in **Appendix B**).

A plot of the absolute efficiency for the coaxial IG detector *versus* photopeak energy shows that the detector is most efficient at photopeak energies <100 keV and that there is a good log-linear relationship of efficiency *versus* energy at energies greater than 100 keV. It was also observed that efficiency was inversely proportional to sample height in the container for the lowest energy peak measured (^{210}Pb = 46.5 keV) as a result of both self-absorption (discussed below) and geometry effects. Self-absorption had no apparent effect on efficiency for the higher energy peaks (such as 351.9 keV and 609.3 keV) which both responded to a change in packing height with similar slopes . Although geometry changes with packing height in large containers were documented, sufficient sample sizes were used for all bulk analyses reported here such that no geometry corrections were necessary, i.e., only full containers with nearly identical geometries were analyzed.

Self-absorption of low energy (energies below about 200 keV) X-rays and γ rays has a significant effect on the apparent efficiencies calculated for the coaxial IG detector in this energy range. Self-absorption corrections must be carefully applied for the ^{210}Pb peak at 46.5 keV and for the measurements of ^{234}Th at 63.3 and 93.1 keV. Since the attenuation for low energy gamma rays is highly dependent upon sample composition, a simple method which can easily correct for self-absorption on a sample-to-sample basis without knowledge of the chemical composition is required for direct analysis by γ spectrometry. The following approach was modified

from that suggested by Cutshall et al., (1983). For a transmitted beam of γ-rays, attenuation will follow the equation:

$$T = Ie^{-\mu\rho x}$$

In which T and I are the attenuated and unattenuated beam intensities, μ is the total attenuation coefficient (cm^2/g), ρ is the material density (g/cm^3) and x is the path length (cm). The self-absorption equation may be written:

$$O = A\,(1-e^{-\mu\rho x})/(\mu\rho x)$$

where O is the attenuated sample output (count rate) and A is the actual sample photon emission rate. To obtain a correction factor for self-absorption, T and I may be measured and the ratio A/O computed from:

$$A/O = \ln(T/I)/(T/I-1)$$

In this work, the attenuated beam intensity T at any one energy was defined as the difference between the count rate of each sample with and without an external source containing ^{210}Pb and natural U centered on top of the sample container. We currently use a plexiglass "hockey puck" that contains a high activity ^{210}Pb foil source and also about 30 grams of uranyl acetate to provide a relatively high activity source. The factor "I" was determined by making a measurement with the same external ^{210}Pb and ^{234}Th (^{238}U) source (the "hockey puck") on top of an empty container. We now find that it is more efficient to define "I" as transmission through the efficiency standard and "T" as transmission through the unknown sample. Gyp-6, a phosphogypsum sample that had been very well characterized, was used as a secondary standard to obtain the apparent (uncorrected) efficiency for the 46.5 and 63.2 keV peaks for the coaxial IG detector. Relative absorption factors (fabs) for all samples were then calculated by dividing the measured correction factors (A/O) for each sample by the same correction factor in the secondary standard (Gyp-6). This ratio thus represents how each sample compares to the efficiency standard in terms of self-absorption. Relative absorption factors were close to unity for all the phosphogypsum samples analyzed here with a range from 0.89 to 1.14. The final ^{210}Pb and ^{234}Th activities were then obtained by substituting the relative absorption factors into the activity calculation equation (Rim and Burnett, 1983):

$$\mathbf{A\ (dpm/g) = (cpm-bgd)*fabs/(Wt*fg*f_i*f_{eff})}$$

where:

- A = activity
- Wt = sample weight in grams;
- f_g = geometry factor;
- f_i = intensity factor; and
- f_{eff} = efficiency of 46.5 keV photopeak.

When this method is applied to the analysis of IAEA-306, a deep-sea sediment supplied by the International Atomic Energy Agency and used as an international intercomparison sample for ^{210}Pb, ^{238}U, and other radionuclides, good agreement with the "recommended" values was obtained Table 3. Absorption corrections are virtually identical for numerous analyses of the same sample as expected. All ^{210}Pb and ^{238}U values for bulk samples reported here have been corrected according to this scheme while activities of higher energy nuclides (>200 keV) have been assessed without an absorption correction.

Activities of ^{238}U in 29 samples of phosphogypsum and ore rocks have been analyzed using both gamma and alpha spectrometry and results from the two techniques are plotted in Figure **1-8.** Activities of ^{238}U range from less than 2 to 119 dpm/g and the effective packing densities are about 0.8 to 2.0 g/cm^3 for this set of phosphogypsum and ore rock samples. The correlation factor (r^2) of 0.996 and the 1.00 slope of the line regressed through the data indicate that the method we use for correcting the attenuation of the low energy (<200 keV) gamma rays works quite well over a range of activities and packing densities. The "error bars" representative of counting uncertainties at the 1σ level are less than the symbol radius until ^{238}U activities are 50 dpm/g or greater in samples that are mostly ore rocks. Generally, uncertainties in alpha spectrometry results for ore rocks were comparable or greater than those of gamma spectrometry. This was partially due to lower chemical yields of U for some of these samples. Poor yields can result from elevated phosphate activities in the sample which cause matrix effects and loss of U from the ion chromatographic resin we use for separating U and Th isotopes. Some scatter in samples plotting above 50 dpm/g in Figure 1-8 may result from using limited quantities of samples (0.3 g) for alpha spectrometry which may not be sufficiently homogenous to be representative of 100 to 200 g of the sample which were packed into the 100 cc aluminum cans and measured by gamma spectrometry.

Overall the method of measuring ^{234}Th in bulk samples and applying an absorption correction factor that is directly related to sample density (Burnett *et al.*, 1993; Oresegun *et al.*, 1993) has proved to be very successful. The advantages of using this technique are that the ^{238}U can be indirectly measured for a sample concurrently with ^{210}Pb, ^{226}Ra and ^{228}Ra with very little additional work. The attenuation measurements for ^{234}Th as well as other nuclides of interest which have gamma energies with photopeak energies of <200 keV can be made concurrently with that of ^{210}Pb so an additional attenuation measurement is not required. Absorption corrected results are comparable to those obtained for ^{238}U by alpha spectrometry which is very time consuming, laborious, and requires an entire alpha spectrometry system and data reduction software. One disadvantage of measuring ^{234}Th directly by gamma spectrometry is that samples which have been chemically processed within the preceding six months may have U and Th isotopes which have been fractionated and are not in radioactive equilibrium and the ^{234}Th

Table 3. Natural uranium and thorium decay-series nuclides measured on the coaxial IG detector for the IAEA-306 intercomparison sample seven times during this study. Errors shown for individual analyses are 1σ based on counting statistics. Means are given and 1 standard deviation of individual counts are also shown. All ^{210}Pb values corrected to reference date of 1 January 1988 and ^{210}Pb and ^{234}Th activities are absorption corrected. The "confidence interval," defined by IAEA, brackets the median value at the 95% confidence level (2σ).

Analysis	^{210}Pb 46.5 keV	$^{238}U(^{234}Th)$ 63.2keV	^{226}Ra*	$^{228}Ra(^{228}Ac)$ 338.4keV	Date counted
1	29.5±0.2	4.9±0.1	3.8±0.1	2.8±0.1	11/12/91
2	28.8±0.3	5.3±0.2	3.5±0.1	2.8±0.1	03/16/92
3	29.4±0.4	4.9±0.2	3.6±0.1	2.6±0.1	03/29/92
4	28.7±0.3	4.4±0.1	3.9±0.1	2.9±0.1	05/26/92
5	27.7±0.1	4.3±0.1	3.6±0.1	2.8±0.1	10/30/92
6	29.2±0.2	4.0±0.2	4.0±0.1	2.9±0.2	03/04/93
7	28.5±0.3	4.6±0.2	4.4±0.1	3.1±0.1	06/04/94
Mean & 1 SD	28.8±0.6	4.6±0.4	3.8±0.3	2.8±0.2	
"Recommended" values**					
Median	26.6	4.6	4.0	2.9	
Confidence Interval (α=0.05)	22.9-32.1	3.9-5.7	3.6-4.9	2.3-4.9	

* ^{226}Ra determined by mean of photopeaks for ^{214}Pb at 295.2 and 351.9 keV, and the 609.3 keV peak of ^{214}Bi.

** Ballestra *et al.*, 1989.

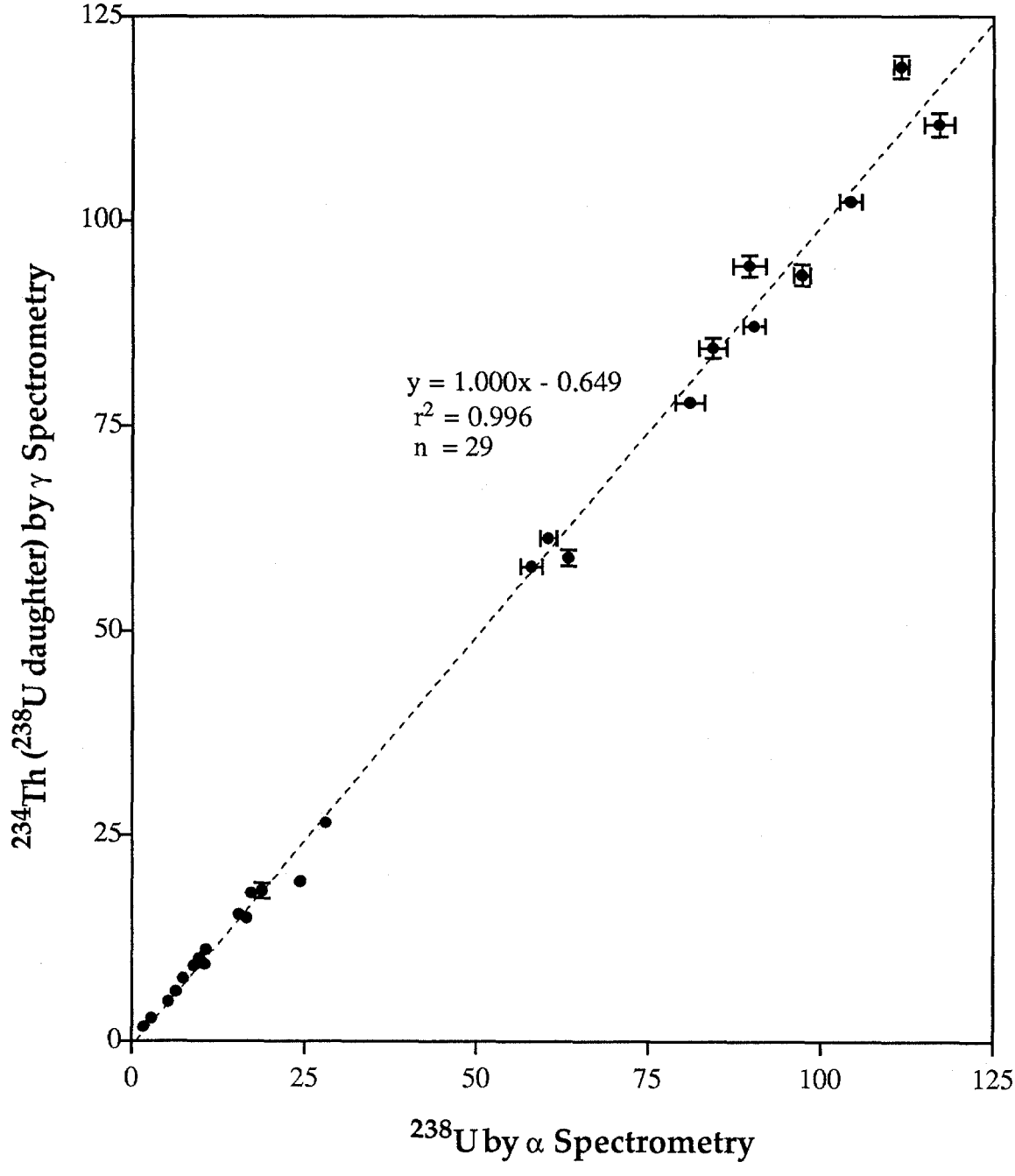

Fig. 1-8 Plot of ^{238}U activities measured by γ-ray spectrometry *versus* ^{238}U activities determined by isotope dilution α-spectrometry. All activities are in dpm/g.

must be allowed to attain secular equilibrium with its parent ^{238}U. An additional drawback is that only ^{238}U is measured by gamma spectrometry and not other U isotopes in the samples. We feel that in some circumstances the benefits of this technique far outweigh the shortcomings.

Isotope Dilution Alpha Spectrometry

Isotope -dilution alpha spectrometry was used to determine quantitatively the activities of ^{210}Po for every sample and ^{238}U, ^{234}U, ^{230}Th, and ^{232}Th for selected samples of Florida ore rocks and phosphogypsum. This well-known method is based on measuring the alpha-activity of isolated and chemically purified radionuclides. Chemical yields are determined by the addition of a known activity tracer. Our laboratory uses ^{209}Po for polonium samples and ^{232}U and ^{228}Th for uranium and thorium isotopes.

Uranium and thorium isotopes were measured following total dissolution of the sample. Accurately weighed ~1 gram samples of phosphogypsum and ~0.35 gram samples of ore rock were dissolved in 750 mL of 4M HCl and 1.000 mL of ^{232}U-^{228}Th spike and 10 mg Fe were added. After 16 - 24 hours to allow for dissolution of gypsum and isotopic equilibration of the spike, solution pH was raised to 6, and hydroxides were scavenged. The ferric and other hydroxides were rinse in deionized water, and redissolved in 4M HCl. This process was repeated three to four times until hydroxide scavenges were mostly $Fe(OH)_3$. The final scavenge was acidified with 2M HCl and the soluble fraction was decanted off. Any solids which remained were centrifuged and transferred to a graphite bottomed Teflon beaker, rinsed with DDW and evaporated to near dryness. The solids were then fumed with HF, $HClO_4$, HNO_3, H_2O_2, and a 3% boric acid solution until all quartz and refractory and highly insoluble phases (ilmenite, zircon, calcium and lanthanum group fluorides, alumuniofluorides) were completely dissolved. Two mL concentrated HNO_3 were added and evaporated to near dryness again to remove excess $HClO_4$ and HF. The two solutions were combined, again scavenged with $Fe(OH)_3$, and dissolved in 2M HNO_3. U and Th were separated with ion chromatographic resin (TRU-Spec™), and then electrodeposited on stainless steel planchets for counting on very low background, ion-implanted alpha detectors.

Samples for ^{210}Po analyses were processed and Po was separated from ^{210}Pb and ^{210}Bi within a few weeks of collection. Ore and phosphogypsum samples were dissolved in an acid digestion bomb with 2 mL concentrated HCl, 3 mL concentrated HNO_3, 1 mL concentrated HF, 0.5 mL concentrated $HClO_4$, and 1.000 mL ^{209}Po tracer. Samples were heated overnight in sealed bombs at approximately 140°C. Ore rocks were processing in a manner similar to U and Th samples. After removing a phosphogypsum sample from an acid bomb, about 3.5 grams K_2CO_3 and 20 mL DDW were added and the sample was refluxed twice to convert the insoluble

$CaSO_4 \cdot nH_20$ to HCl-soluble $CaCO_3$. The sample was transferred to a centrifuge tube and washed with DDW until pH=7 was reached to remove all excess carbonate and sulfate from the sample. The precipitate was totally dissolved with approximately 2 mL of concentrated HCl. At this point, 10 mg of Fe carrier was added and $Fe(OH)_3$ precipitated with ammonium hydroxide, the solids were centrifuged, washed, decanted, and finally dissolved in 2M HCl. Any solids remaining were treated as described above for U and Th samples and the solution was scavenged, redissolved in 2M HCl, and Po solutions were recombined.

At this point Po samples were totally dissolved and ready for source preparation either by electrodeposition or spontaneous plating. Most Po sources were prepared by spontaneous plating of polonium from an acidic solution onto pure silver discs by the method described by Harada et al. (1989). For polonium electrodeposition, a 24-mm polished stainless steel disc was plated with a thin layer of copper in a cell containing around 50 mg $CuSO_4$ in 1M H_2SO_4 for about 10 seconds at 2.6 volts. When spiral marks were apparent on the disc, they were polished off by rubbing the disc once or twice on a 600 grit polishing strip and then electrodeposited again. One gram of ascorbic acid and 1.5 grams of hydroxylamine hydrochloride were added and polonium was electrodeposited onto the copper-coated discs at 1.1 volts for 90 minutes. The surface of the discs were then washed as it emerged from the plating solution by using the elongated and curved tip of a washbottle to prevent acid staining of the disk surface.

All prepared sources for alpha spectrometry were then counted in one of several low-background alpha spectrometers routed to a Canberra Series 95 Multi-Channel Analyzer. Backgrounds of the alpha spectrometers used for this study ranged from 0.004 to 0.011 cpm with an average of approximately 0.007 cpm for the ^{210}Po peak, and ranged from 0.013 to 0.034 cpm with an average of approximately 0.02 cpm for the ^{209}Po peak. Reagent blanks averaged about 0.01 cpm above background for both the ^{210}Po and ^{209}Po peaks. Data reduction was performed by a customized computer program that includes provisions for decay corrections and error propagation due to counting statistics.

RESULTS AND DISCUSSION

Radionuclides in Ore Rocks and Phosphogypsum

Radionuclide activities have been measured for seventy-eight samples of Florida phosphogypsum and seventeen phosphate ore rocks. A statistical summary of these results is given in Table 4. Replicate samples were occasionally performed for ^{210}Po analyses and ^{210}Po activities are decay/ingrowth corrected to the date of collection. Activities measured for replicate and recounted samples were averaged before use in the statistical summary and uncertainties for both types of measurements were propagated accordingly. Activities of ^{210}Po in some samples of

Table 4. Statistical summary of radiochemcial results for Florida phosphogypsum and phosphate rock samples.

Radionuclide	^{238}U	^{226}Ra	^{210}Pb	^{210}Po	(^{210}Pb/ ^{226}Ra)	(^{210}Po/ ^{210}Pb)
	Specific Activities Given in dpm/g					
Phosphogypsum - Central & Southern Florida Dihydrate						
Mean	7.9	54.4	51.6	51.6	0.95	1.00
Stan. Deviation (1σ)	5.1	11.3	11.9	12.2	0.13	0.17
Range	2.4-22.1	30.3-81.2	34.7-110.0	26.1-105.9	0.66-1.37	0.68-1.65
No. of Analyses	97	98	97	82		
Phosphogypsum - Northern Florida Hemihydrate						
Mean	7.8	26.0	26.1	25.6	1.01	0.98
Stan. Deviation (1σ)	8.0	7.5	4.5	4.1	0.15	0.10
Range	1.4-27.1	16.2-35.9	20.8-33.2	21.3-34.0	0.78-1.28	0.74-1.08
No. of Analyses	13	13	13	10		
Phosphate Rock - Central & Southern Florida						
Mean	75.8	87.6	86.5	81.3	0.99	0.94
Stan. Deviation (1σ)	26.5	17.2	15.8	16.5	0.06	0.03
Range	50.9-118.8	52.9-118.8	52.9-110.1	52.3-110.1	0.94-1.16	0.93-1.08
No. of Analyses	21	21	21	24		
Phosphate Rock (Northern Florida)						
Mean	41.5	38.5	41.4	38.9	1.07	0.94
Stan. Deviation (1σ)	21.2	18.4	20.8	18.0	0.05	0.07
Range	14.5-58.9	13.8-53.0	14.4-58.9	14.3-52.6	1.01-1.13	0.89-1.03
No. of Analyses	4	4	4	4		

phosphogypsum collected <3 years from production were not in secular equilibrium with parent ^{210}Pb. Replicate analyses for these samples were conducted during the ingrowth period to confirm that ^{210}Po approached equilibrium. Detailed descriptions of all samples collected for this study are given in Appendix A and the complete radioanalytical database is presented in **Appendix B.**

Detailed radiochemical analyses of long-lived radionuclides in the ^{238}U decay-chain and ^{232}Th for a sub-set of 17 representative samples of phosphogypsum and 11 phosphate rock samples from Florida are given in **Table 5**. Eleven of the fresh phosphogypsum samples shown in Table 5 were collected in pairs with ore rock that was being reacted when samples were collected. The approximate percentage of a radionuclide that fractionated to the phospho-gypsum for these 11 ore rock - phosphogypsum pairs are listed in **Table 6**. Ideal mass ratios are applied in these calculations, so percentage data must be considered rough estimates. It is clear that the reaction is far from ideal and unreacted materials introduce significant uncertainties that are not accounted for in these data.

The phosphate rock samples from central and southern Florida display ^{238}U and daughter activities in the range 50-110 dpm/g (Tables 4 and 5). Ores from northeastern Florida contain less than half the activity of all these nuclides as do the corresponding phosphogypsum samples. This is a direct reflection of the raw material being processed there because the rock used for production of phosphatic fertilizer contains significantly lower level of radionuclides. These results confirm that the various members of ^{238}U decay chain, including ^{238}U, ^{230}Th, ^{226}Ra, ^{210}Pb, and ^{210}Po, are in approximate radioactive equilibrium in phosphate rock. It is clear that this equilibrium is significantly disrupted during the chemical manufacture of phosphoric acid.

This disruption is evidenced in Tables 4, 5, and 6 and is clearly shown in **Figure 1-9** which displays plots of ^{238}U, ^{230}Th, ^{226}Ra, ^{210}Pb, ^{210}Po in 12 phosphogypsum samples *versus* activities in the corresponding phosphate rock. The activities of ^{226}Ra, ^{210}Pb, and ^{210}Po in phosphogypsum display good correlation's versus activities of the corresponding phosphate rock. The rock: gypsum mass ratio of ~1:1.7 can be factored with slopes for the regressed lines in these plots to give a rough percentage of the nuclide that reports to phosphogypsum. Results are 81 to 95% for Pb, Ra, and Po in the gypsum when the data are smoothed in this way. That the great majority of ^{226}Ra remains with the phosphogypsum has been well established, but these results demonstrate that virtually all ^{210}Pb and ^{210}Po are also present in fresh phosphogypsum as well (Table 5). It most cases the activities of ^{226}Ra, ^{210}Pb, and to a lessor extent, ^{210}Po in fresh phosphogypsum are directly and predictably proportional to the activities in the input phosphate rock, indicating that the extent of incorporation of these nuclides into the phosphogypsum is primarily controlled by the amount supplied by the ore rock.

Table 5. Radiochemical analyses of long-lived radionuclides in the ^{238}U decay-chain and ^{232}Th for selected samples of phosphogypsum and phosphate rock. Activities of ^{238}U, ^{234}U, ^{230}Th, ^{232}Th, and ^{210}Po activities were measured by α -spectrometry and ^{226}Ra and ^{210}Pb by γ-spectrometry. Two or more α spectrometric analyses have been performed for replicates of selected samples. Uncertainties are given at the 1 σ level based on counting statistics only.

Sample ID	^{238}U dpm/g	^{234}U dpm/g	^{230}Th dpm/g	^{226}Ra dpm/g	^{210}Pb dpm/g	^{210}Po dpm/g	^{232}Th dpm/g
			Phosphogypsum Samples				
Gyp-8	16.2±0.3 17.0±0.6	16.1±0.3 18.5±0.7	19.3±0.2 19.6±0.3	46.9±0.3	45.9±0.7	45.3±0.6	0.14±0.02 0.61±0.08
Gyp-10	1.73±0.08	13.1±0.3	17.2±0.2	16.2±0.2 16.1±0.2	20.6±0.4 20.9±0.5	21.9±0.4	0.69±0.05
Gyp-13	6.4±0.1	6.5±0.1	12.4±0.1 12.2±0.1	44.8±0.2	44.7±0.5	46.2±0.6	0.64±0.03 0.50±0.02
Gyp-18	9.1±0.4 9.1±0.3	10.8±0.5 9.6±0.3	8.8±0.1 9.2±0.3	53.5±0.3 51.6±0.4	49.2±0.7 48.9±0.9	54.3±0.9 55.8±0.6	0.18±0.02 0.17±0.04
Gyp-19	9.8±0.3	9.5±0.3	6.8±0.1	32.7±0.2 33.3±0.3	34.9±0.5 34.5±0.7	33.9±0.6	0.25±0.03

Table 5 (continued)

Sample ID	^{238}U dpm/g	^{234}U dpm/g	^{230}Th dpm/g	^{226}Ra dpm/g	^{210}Pb dpm/g	^{210}Po dpm/g	^{232}Th dpm/g
Gyp-21	10.0±0.2	10.2±0.2	8.2±0.1 7.6±0.1	57.7±0.4 59.6±0.5	60.7±0.8 59.7±1.0	69.1±0.9 71.4±0.9 70.6±0.5 62.8±0.5	0.17±0.01 0.12±0.01
Gyp-26	15.5±0.2	15.8±0.2	11.7±0.2	44.2±0.2 44.5±0.4	50.6±0.5 50.8±0.8	51.8±0.4	0.21±0.03
Gyp-30	9.6±0.2 9.0±0.3	9.9±0.2 9.3±0.3	7.3±0.2 7.0±0.1 7.1±0.1	46.4±0.4 45.0±0.3	51.0±0.7 51.0±0.7	38.8±0.4	0.24±0.05 0.25±0.01 0.20±0.01
Gyp-31	10.7±0.1	11.9±0.1	8.9±0.3	72.2±0.4 70.4±0.4	62.2±0.8 63.1±0.9	72.6±0.6	0.35±0.05
Gyp-34	10.6±0.3	10.8±0.4	5.4±0.1	57.8±0.3 55.3±0.4	54.7±0.5 57.0±0.8	51.9±0.6	0.12±0.02
Gyp-38	24.4±0.5	24.2±0.5	19.6±0.3	44.8±0.3 49.9±0.2	50.1±0.8 46.5±0.6	56.5±0.6	0.50±0.05
Gyp-43	2.8±0.1	4.1±0.1	18.1±0.2	65.7±0.2	57.1±0.5	56.4±1.0	0.30±0.03

Table 5 (continued)

Sample ID	^{238}U dpm/g	^{234}U dpm/g	^{230}Th dpm/g	^{226}Ra dpm/g	^{210}Pb dpm/g	^{210}Po dpm/g	^{232}Th dpm/g
Gyp-47	19.8±0.7 17.9±0.6	20.1±0.7 23.1±0.8	14.3±0.2 14.1±0.2	66.2±0.3 64.9±0.4	57.2±0.6 55.4±0.9	59.1±0.5	0.15±0.02 0.41±0.04
Gyp-48	17.3±0.4	16.8±0.4	18.0±0.2	68.1±0.3 68.0±0.3	56.5±0.8 56.6±0.8	63.1±0.9	0.24±0.02
Gyp-53	7.5±0.2	7.7±0.2	8.4±0.1	36.0±0.2 35.7±0.3	27.9±0.4 27.8±0.6	30.2±0.5	.59±0.04
Gyp-54	28.1±0.7	28.2±0.7	30.8±0.3	34.7±0.2 34.4±0.2	33.2±0.5 32.2±0.5	34.0±0.9	1.34±0.07
Gyp-57	9.0±0.2	11.9±0.2	26.7±0.3	19.4±0.2	23.0±0.5	23.0±0.3	1.11±0.05
			Phosphate Rock Samples				
OreS-18	84.3±2.0	87.7±2.1	84.0±0.8	80.9±0.3	80.3±1.1 82.8±2.5	77.8±1.4	1.75±0.12
OreS-19	60.4±1.2	63.1±1.3	61.1±0.8	56.4±0.2	56.2±0.7	57.8±0.5 54.9±1.0	2.20±0.16
OreS-21	102.6±2.5 106.0±2.2	105.2±2.6 113.4±2.4	104.3±1.0 108.5±1.2	99.9±0.4	94.4±1.2	93.4±2.1 97.8±1.6	0.66±0.08 0.85±0.11

Table 5 (continued)

Sample ID	^{238}U dpm/g	^{234}U dpm/g	^{230}Th dpm/g	^{226}Ra dpm/g	^{210}Pb dpm/g	^{210}Po dpm/g	^{232}Th dpm/g
OreS-26	97.2±1.2	98.9±1.3	93.9±0.9	94.3±0.3 91.2±0.4	88.8±0.9 91.2±1.3	88.5±1.6	1.62±0.12
OreS-31	111.6±1.1	131.0±1.3	117.4±0.7	113.7±0.4	109.9±1.4	110.1±1.6	0.76±0.06
OreS-34	89.6±2.4	89.6±2.4	93.1±1.0	94.7±0.2 91.7±0.4	86.7±0.5 91.4±1.3	87.4±0.8	2.14±0.16
OreS-38	81.0±2.1	79.9±2.0	76.0±1.3	69.8±0.2	80.9±0.8	87.4±0.8	2.10±0.21
OreS-47	90.3±1.6	90.8±1.6	96.3±0.7	55.0±0.2	59.4±0.8	61.2±1.1	0.66±0.06
Ore48	117.1±2.2	124.2±2.3	114.1±0.8	97.7±0.4	110.1±1.6	102.5±1.2	0.81±0.07
Ore-53	57.9±1.6	59.1±1.6	58.6±0.5	52.0±0.2	58.9±0.7	52.6±1.0	3.24±0.12
Ore-54	63.3±1.0	68.7±1.1	52.0±0.6	53.0±0.3	56.7±1.0	52.0±1.2	2.05±0.13

Table 6. Percentages of radionuclides in the ^{238}U decay-chain which report to the phosphogypsums which are produced when the corresponding ore rocks are acidulated assuming a mass difference of ~1:1.71 for calcium fluorapatite to the dihydrated form and ~1:1.44 to the hemihydrated form of phosphogypsum. Mean values are used when two or more analyses have been produced for a nuclide. Uncertainties are propagated at the 1 σ level. See text for discussion.

Ore Rock - Gypsum Pair	Percentages of Radionuclides Reporting to Phosphogypsum					
	% of ^{238}U	% of ^{234}U	% of ^{230}Th	% of ^{226}Ra	% of ^{210}Pb	% of ^{210}Po
18	18.5±1.1	19.9±1.3	18.3±0.6	111.2±1.4	102.9±3.6	121.1±4.2
19	27.7±1.7	25.7±1.7	19.0±0.6	100.1±1.1	105.6±3.2	103.1±3.6
21	16.4±0.7	16.0±0.7	12.7±0.3	100.4±1.0	109.1±2.3	112.3±3.1
26	27.3±0.8	27.3±0.9	21.3±0.7	81.8±0.8	96.3±2.1	100.1±3.4
31	16.4±0.4	15.5±0.3	13.0±0.8	107.2±1.0	97.5±2.7	112.8±3.2
34	20.2±1.3	20.6±1.6	9.9±0.4	103.8±0.9	107.2±2.1	101.5±2.6
38	51.5±2.9	51.8±2.9	44.1±1.7	116.0±1.0	102.1±2.6	110.5±2.7
48	25.3±1.3	23.1±1.2	27.0±0.6	119.1±1.0	87.8±2.6	105.35±3.3
53	22.2±1.5	22.3±1.4	24.5±0.6	117.9±1.3	80.9±2.4	98.2±4.2
54*	63.9±1.9	59.0±1.7	85.2±1.3	93.9±0.7	83.1±1.7	94.2±3.3

*Gyp-54 is a hemihydrate.

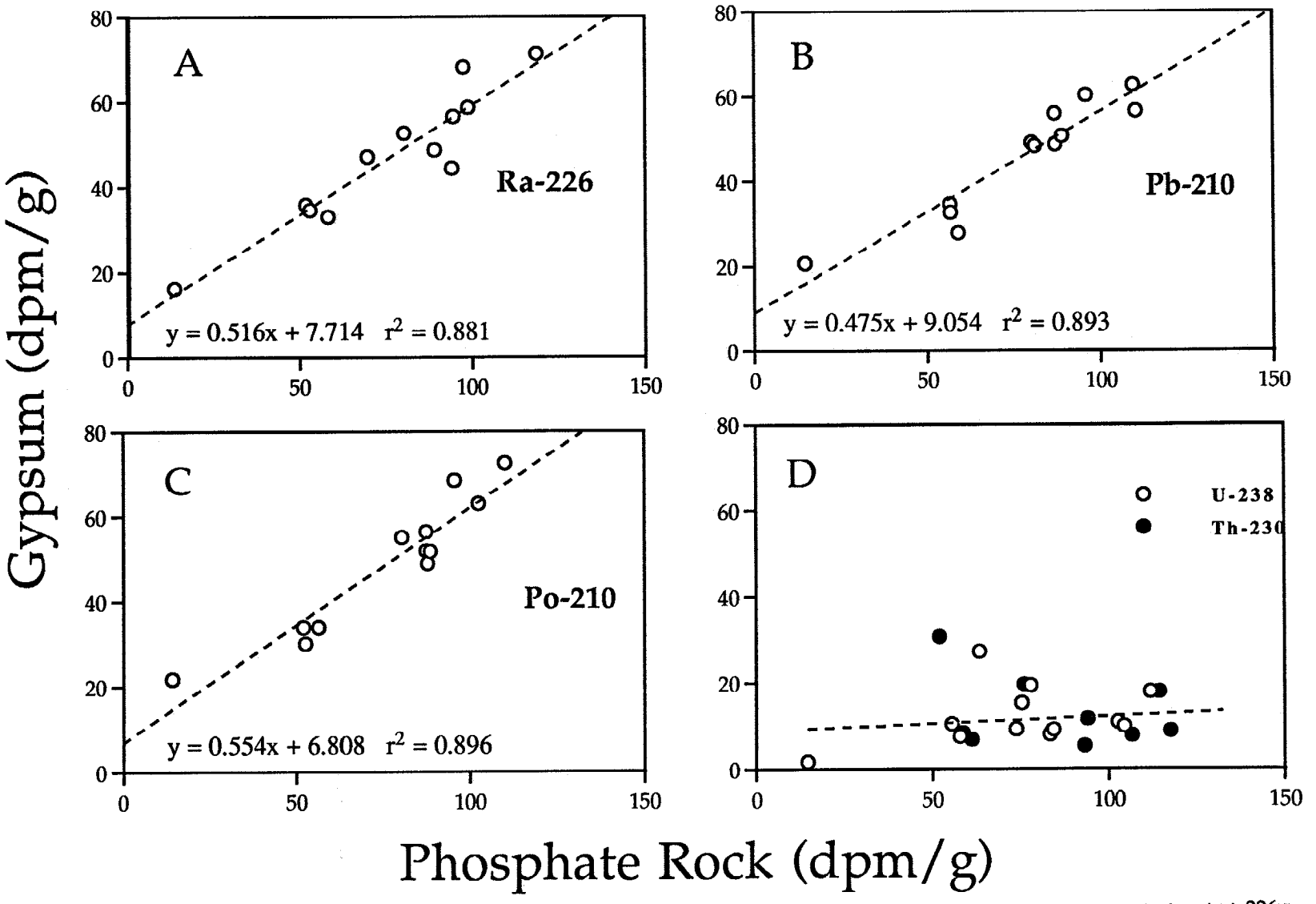

Fig. 1-9 Relationships of activities of uranium-series radionuclides in gypsum *versus* phosphate rock for (A) ^{226}Ra; (B) ^{210}Pb; (C) ^{210}Po; and (D) ^{238}U and ^{230}Th. Least squares regression lines shown for ^{226}Ra, ^{210}Pb, and ^{210}Po.

Uranium and Thorium Nuclides

The great majority of ^{226}Ra ^{210}Pb, and ^{210}Po are incorporated in the phosphogypsum, but the partitioning of ^{230}Th and ^{238}U is more variable. The dissolved uranium is largely incorporated in the acid phase as uranyl phosphate, sulfate, and fluoride complexes. Any tetravalent uranium which is in the phosphate rock is oxidized to U^{6+} during the acidulation process and uranyl ions are predominately complexed with phosphates. Many fertilizer production facilities have, at one time or another, recovered U from acid for sale to the nuclear industry so the reaction and speciation of U in phosphoric acid is fairly well understood. However, up to 50 - 60% of U fractionated to phosphogypsum in samples given in Table 6 demonstrate that the redistribution of ^{238}U and ^{230}Th during acidulation of phosphate rock may be controlled by a number of factors. Some of these factors include redox potential and digestion temperature during the processing of phosphate rock, sorption on humic substances and clays, coprecipitation with fluorides, etc. The ^{238}U content of the by-product gypsum shows no significant correlation to the ^{238}U content of the phosphate rock ($r^2<0.11$ in Figure 1-9) and may simply be related to the extent of unreacted ore and oversaturation and re-precipitation of calcium fluorapatite which is known to occur in production processes. The presence of chuvkhrovite and other complex Fe phosphates, fluorosilicates, and fluorite documented by Kennedy *et al.* (1991) for phosphogypsum slurries and process waters was confirmed in XRD patterns of leached phosphogypsum samples collected for this study. We have also identified U-bearing resistate minerals such as Fe-Ti oxides, various polymorphs of iron and aluminum phosphates the high U phase in weathered ore deposits) in bulk phosphogypsum using XRD.

Radium

Radium, which exhibits a chemical behavior similar to calcium in these systems (Roessler, 1988; Lardinoye *et al.*, 1982) has been proposed to: (1) coprecipitate as some yet unknown phase or solid solution with $CaSO_4 \cdot nH_2O$ (Roessler, 1990); (2) be included in radiobarite ($BaSO_4$ containing radium) or $(Ba,Sr)SO_4$ solid solutions (Moisset, 1988; 1990; Rutherford *et al.*, in press); and (3) be sorbed on organic material (Ferguson, 1985). It is not definitively known how ^{226}Ra is included in phosphogypsum and this topic is addressed further in Chapter 2 of this report. It may be that a combination of these and other processes control ^{226}Ra solubility in phosphogypsum. Although the site(s) occupied by ^{226}Ra are not well characterized, it is clear from data presented in Table 6 and from studies by Roessler **et al.**, (1979), Lardinoye *et al.*, (1982), and results presented here that virtually all ^{226}Ra in phosphate ore rock fractionates to phosphogypsum.

The summary of activity data (Table 4) lists mean values for ($^{210}Pb/^{226}Ra$) in phosphogypsum produced from ores in both phosphate districts. Both are near

unity, but values range from 0.66 to 1.37. Ratios that are slightly less than 1 can be explained by Rn loss, but when ($^{210}Pb/^{226}Ra$) is less than 0.85, it is likely that ^{226}Ra must be added to the sample or ^{210}Pb was lost and vice versa when ($^{210}Pb/^{226}Ra$) is greater than 1.1. Based on studies of the behavior of ^{226}Ra in leached phosphogypsum samples (Rutherford et al., in press; Chapter 2 of this report) Ra is relatively immobile on the unsaturated, aerobic portions of gypsum stacks in comparison to ^{210}Pb. However, process and cooling pond waters at fertilizer production facilities may contain appreciable activities of ^{226}Ra (eg. 121 dpm/L, 190 dpm/L, and 149 dpm/L at one facility sampled in 1979, 1988, and 1994; Florida DEP unpublished data). Fresh phosphogypsum slurries being discharged onto stacks are made up of 75 to 80% of cooling pond water so the possibility exists for addition of radionuclides, especially in freshly discharged phosphogypsum.

Lead and Polonium

The other main radionuclides which are found in phosphogypsum, ^{210}Pb and ^{210}Po, are present in all samples including fresh samples collected directly from gypsum discharge pipes at phosphoric acid plants. Since the activities of ^{210}Pb and ^{210}Po are generally comparable to ^{226}Ra (Table 4), the predominant source of these nuclides must be the phosphate rock instead of accumulating as decay products of ^{226}Ra during gypsum storage (Roessler, 1984). The half-lives of ^{210}Pb (22.3 years) and ^{210}Po (138.4 days) are such that ingrowth periods of approximately 100 years for ^{210}Pb and 2 years for ^{210}Po would be necessary to obtain secular equilibrium by ingrowth.

When the ($^{210}Pb/^{226}Ra$) activity ratios for individual samples are examined, most display a few percent deficiency in ^{210}Pb which can be attributed to radon loss in older samples. During the analyses of these gypsum samples, it was discovered that larger radon losses, on the order of 30% or more of the radon, would occur over short time periods (sample preparation). The long-term, less than 10% loss based on the ^{210}Pb activities implies that radon emanation in the field is much less important than may be implied by "emanation coefficients" as measured in the laboratory. Two of the 25 fresh phosphogypsum samples have ($^{210}Pb/^{226}Ra$) less than 0.85 and 4 other fresh samples with slightly higher ratios suggest that the ($^{210}Pb/^{226}Ra$) in cooling pond waters used to slurry the by-product may influence activity ratios in some younger samples. Activity ratios ($^{210}Pb/^{226}Ra$) less than 0.85 in 5 of 53 older samples could result from either or a combination of the processes described above or by Pb loss from the sample during storage. In 4 of these 5 older samples, ($^{210}Po/^{210}Pb$) is near unity so if Pb was leached from the sample, the leaching ceased >3 years before sampling. An older phosphogypsum sample (Gyp-51) shows evidence for leaching of Pb within 2 years of collection as evidenced by ($^{210}Pb/^{226}Ra$) of 0.66 and ($^{210}Po/^{210}Pb$) of 1.57 (Appendix B).

Twelve of the 78 phosphogypsum samples (Gyp-9, Gyp-10, Gyp-17, Gyp-26, Gyp-29, Gyp-30, Gyp-38, Gyp-39, Gyp-45, Gyp-46, Gyp-50, and Gyp-57), have ^{210}Pb activities significantly above ^{226}Ra ($^{210}Pb/^{226}Ra$ greater than 1.1) implying that either ^{210}Pb is preferentially scavenged relative to ^{226}Ra, the ($^{210}Pb/^{226}Ra$) of the slurry water may have influenced the ratio in the sample, or that there is migration of ^{210}Pb and/or ^{226}Ra in solutions within gypsum stacks. Of the 12 samples with significant amounts of excess ^{210}Pb, 5 are fresh (no more than weeks old) while the remainder are years to decades old. In the 25 samples of freshly produced phosphogypsums, only 5 had ($^{210}Pb/^{226}Ra$) greater than 1.1 and 18 fresh samples all had ($^{210}Pb/^{226}Ra$) between 0.88-1.05. It seems that excess ^{210}Pb could be added with process water, but ($^{210}Pb/^{226}Ra$) in fresh samples are most influenced by the ratio in the ore rock. Two samples that had been on stacks for a number of years (Gyp-9 and Gyp-45) had ($^{210}Pb/^{226}Ra$) of 1.20 and 1.22 whereas ($^{210}Po/^{210}Pb$) at the date of collection 0.71 and 0.83 which clearly demonstrates that ^{210}Pb had been added to the samples from solutions percolating through the gypsum stacks sometime during the 2 years preceding collection.

The activities of ^{210}Po and ($^{210}Po/^{210}Pb$) in 25 fresh phosphogypsum samples are quite variable (Appendix B) and show that ^{210}Po closely approaches equilibrium with ^{210}Pb in 10 samples (Gyp-7, Gyp-14, Gyp-15, Gyp-19, Gyp-26, Gyp-34, Gyp-35, Gyp-47, Gyp-50, Gyp-54), is significantly enriched in 9 samples (Gyp-18, Gyp-21, Gyp-22, Gyp-31, Gyp-36, Gyp-38, Gyp-40. Gyp-48, Gyp-53) or depleted in 6 samples (Gyp-23, Gyp-30, Gyp-33, Gyp-39, Gyp-44, Gyp-49) in relation to its ^{210}Pb grandparent. The variability of ^{210}Po activities in fresh phosphogypsum samples, some produced within weeks of one another and deposited in the same region of a gypsum stack, may be related to changes in ore rock compositions, redox potentials and digestion temperatures during the processing of phosphate rock, and the quantity of organic material in the ore. Another factor which undoubtedly impacts ($^{210}Po/^{210}Pb$) in fresh phosphogypsum is the ($^{210}Po/^{210}Pb$) in the cooling water that is used to slurry the by-product for discharge onto the stacks.

The ($^{210}Po/^{210}Pb$) activity ratios for those samples older than two years should be approximately equal to unity since ^{210}Po will reach >97% equilibrium with ^{210}Pb in about five half-lives of ^{210}Po, either by decay of excess ^{210}Po or by ingrowth from ^{210}Pb via ^{210}Bi. However, the activities of ^{210}Po and ^{210}Pb in six phosphogypsum samples that are old enough for ($^{210}Po/^{210}Pb$) to have reached secular equilibrium (Gyp-9, Gyp-18, Gyp-45, Gyp-51, Gyp-52, Gyp-56) do not all have activity ratios of 1.00. Four of the 6 "mature" phosphogypsum samples that do not have ($^{210}Po/^{210}Pb$) between 0.9-1.1 are depleted in ^{210}Po relative to ^{210}Pb (Gyp-9, Gyp-45, Gyp-52, Gyp-55), but the apparent depletion in 3 of these samples (Gyp-9, Gyp-45, Gyp-55) is likely caused by Pb being added to the sample from solutions circulating in the gypsum stack within two years of sample collection. The remaining 2 of these 6 samples

(Gyp-18, Gyp-51) had ($^{210}Po/^{210}Pb$) activity ratios greater than 1.1 and on the date of collection, indicating probable loss of Pb from these samples.

Hurst and Arnold (1982) suggested previously that excess amounts of ^{210}Po are present in phosphogypsum because of more efficient polonium incorporation in the gypsum phase relative to ^{210}Pb. Preferential incorporation of polonium does not seem to be the case in samples we have analyzed since only 9 of the 25 fresh phosphogypsums had excess ^{210}Po and Po migration and addition is not indicated for any of the 53 older phosphogypsums which were collected after various periods of weathering on or near stack surfaces. On the other hand, Pb leaching, mobilization, and re-sorption/precipitation may be the processes responsible for ($^{210}Pb/^{210}Po$) disequilibrium in mature phosphogypsum samples. This interpretation is consistent with some of our groundwater data which shows occasionally very high ^{210}Pb and high ($^{210}Pb/^{210}Po$) activity ratios, especially in some of the more acidic wells (see section on "Monitor Well Waters" below).

We do not know as yet if ^{210}Po is leached and migrates in the saturated, reduced portions of gypsum stacks since all our older samples have been collected at or near the stack surface or from one very shallow well in the P-21 stack. Even though Po is surface reactive under most physiochemical conditions, unsupported ^{210}Po in acidic, reduced groundwaters in areas associated with ore bodies is well documented and has been attributed to the activity of sulfate-reducing bacteria (Harada et al., 1989). Migration of ^{210}Po in gypsum stacks in relation to microbiological factors is discussed in Chapters 3 and 4 of this report.

Radionuclides on Production Filter Screens

The activities of ^{210}Pb, ^{226}Ra, and ^{228}Ra (^{228}Ac) are given in Table 7 for residues on woven polypropylene and glass fiber filter screens that were used to separate phosphoric acid in an phosphoric acid facility in central Florida. These filter screens are known to contain relatively high activities of ^{226}Ra (Keaton, 1987) so we felt there was a high probability that the insoluble phase(s) which contains the great majority of radionuclides in phosphogypsum would be concentrated on such a filter screen. A Geiger-Mueller detector was used to target segments of the filter screen that contained higher activities of radionuclides and these sections of the unwashed filter screen were carefully cut into strips which could be rolled into tubes with the same geometries and inserted into the vials used for our well-type IG detector. Scales deposited on the screen were disturbed as little as possible. An extremely fine-grained scale that is not visible without magnification could not be physically separated from the woven filter substrate. The mass of the filter screen itself is believed to comprise >95% of the total mass contained in the vials.

Barite was positively identified by XRD in a very small sample of scale (Scale #3) that separated from the filter when a portion of the screen was leached in 0.1M

Table 7. Activities of ^{210}Pb, ^{226}Ra, and ^{228}Ra measured in scales removed from production filters and in very fine-grained encrusted scales measured while still on the filter. Errors shown for individual analyses are 1σ and based only on counting statistics.

Sample	Mass (g)*	^{210}Pb 46.5 keV (dpm/g)	^{226}Ra 185.9 keV (dpm/g)	$^{228}Ra(^{228}Ac)$ 338.4keV (dpm/g)	$(^{210}Pb/^{226}Ra)$
Scale 1	1.916	1050±10	2270±10	11±2	0.46±.01
Scale 2	1.585	1330±10	2850±10	19±2	0.47±.01
Scale 3	0.010	5100±200	14000±3000	1400±400	0.35±.01
Filter	0.621	14820±70	34400±100	160±20	0.43±.01

* Masses are of encrusted scale together with dry filter screen except Scale 3 (<0.01 g) that separated from filter during 0.1M HCl leaching.

HCl. This leached scale has the highest specific activity of ^{226}Ra measured during this study (>35,000 dpm/g) (Table 7) so a radiobarite type of phase does exist on this screen. However, these screens are used for filtration for weeks and represent open chemical systems. Although a radiobarite type of mineral phase may contain a portion of the ^{226}Ra in phosphogypsum, barite has yet to be positively identified in phosphogypsum by XRD and SEM techniques.

Monitor Well Waters

The pH, conductivity, temperature, and sulfide concentrations in groundwater samples collected over a two year period from monitoring wells adjacent to seven phosphogypsum stacks are given in **Table 8**. Wells at the P-21 stack were sampled a number of times under various hydrological recharge conditions. Wells near other stacks were sampled only once or periodically to characterize the fluid compositions and activities of ^{226}Ra, ^{222}Rn, ^{210}Pb, and ^{210}Po in solution. Activities in well water samples are given in decay per minute per liter (dpm/L) for these nuclides in **Table 9**.

There is a wide range of pH, electrical conductivity, and sulfide concentrations in surficial groundwaters collected from monitor wells waters adjacent to phosphogypsum stacks in Florida (Table 8). The pH values of well waters are extremely variable. Waters collected from wells in northern Florida at the Occidental facility are near neutral (pH of ~ 6 to 7) and those collected in SW 1 and 2 at the CF Bartow site are quite acidic at pH ~2. Electrical conductivity's of waters from SW 1 and 2 are over an order of magnitude higher in these two well waters than almost all other water samples and are likely caused by higher concentrations of total dissolved solids in these acidic waters. Conductivity's are also relatively high in the Cargill - Tampa MW 1 and 8 and Farmland MW 2 and 5. Sulfide concentrations are elevated in the IMC P-21 wells and Farmland MW 2 and 5. The lack of sulfide in Occidental wells and Cargill - Tampa MW 3 is notable as is the low sulfide concentration in Royster (Mulberry) MW 9. Low sulfide concentrations are not correlatable with higher pH in each instance, but there seems to be an inverse relationship between these two parameters when pH approaches 7 as is expected from Eh - pH diagrams of the S-O-H system (Wagman *et al.*, 1982; Brookins, 1988). It is not clear at this time whether the lack of sulfide is due to well depths and distributions or results from the pH and Eh of the hydrologic systems. However, it is most likely that Eh controls sulfide activities to a much greater degree in the pH range of most groundwaters sampled in this study.

There are also appreciable variations in the activities of radioelements (Table 9). Radon, for example, ranges from relatively low values of 590 dpm/L in one analysis of P-21 MW 16 and 880 dpm/L in Cargill - Tampa Stack MW 8 to over 132,000 dpm/L in the P-21 MW 12. This is not unusual since radon has been proven to vary tremendously over short distances in shallow aquifers because of "source

Table 8. Groundwater parameters from monitor wells near gypsum stacks. Low pH values show that extremely acidic conditions develop within some of these gypsum stacks.

Company	Well ID	Temp. °C	Cond. (µmhos)	pH	Sulfide (µM/L)
		Jan. 8-9, 1991			
Farmland	MW 1	25.9	130	4.45	1
Farmland	MW 3	24.0	110	4.71	12
Farmland	MW 5	26.1	5540	4.75	91
Farm Land	MW 6	--	--	--	73
IMC (P-21)	MW 12	22.0	1320	3.84	40
IMC (P-21)	MW 16	21.6	760	5.44	7
		Feb. 13-14, 1991			
IMC (P-21)	MW 11	26.0	1600	3.73	--
IMC (P-21)	MW 12	23.9	1620	4.18	91
IMC (P-21)	MW 16	24.5	1140	4.53	--
IMC (P-21)	MW 17	24.0	690	3.93	3
Royster	MW 1	22.7	271	6.44	96
Royster	MW 6	23.0	202	5.43	0
Royster	MW6/2	23.0	188	5.33	--
Royster	MW 9	22.3	205	6.78	1
Royster	MW 9/2	23.0	220	7.24	--
		March 25-26, 1991			
IMC (P-21)	MW 12	23.5	1600	4.21	--
IMC (P-21)	MW 16	25.5	1300	4.45	--
CF Industries	SW-1	25.5	40	4.88	--
CF Industries	SW-2	24.0	24800	1.57	--
CF Industries	SW-3	26.0	13000	2.04	--
CF Industries	SW-5	23.6	79	5.56	--
		April 30, 1991			
Occidental	SC 3S	22.6	500	6.76	0
Occidental	SC 4D	22.5	410	6.80	0
Occidental	SC 4S	23.8	1870	6.22	0

Table 8 (Continued)

Company	Well ID	Temp. °C	Cond. (µmhos)	pH	Sulfide (µM/L)
		Jun. 3-4, 1991			
IMC (P-21)	MW 11	24.8	2120	4.82	--
IMC (P-21)	MW 12	24.2	1920	4.14	134
IMC (P-21)	MW 16	24.9	1690	4.40	165
IMC (P-21)	MW 17	24.8	1200	4.20	183
IMC (P-21)	MW 18	26.0	125	5.41	0
Cargill	MW 1	24.8	11200	4.88	100
Cargill	MW 3	25.0	1350	6.70	0
Cargill	MW 8	27.0	17000	5.30	2
		Nov. 7-8, 1991			
IMC (P-21)	MW 12	23.8	1850	4.20	129
IMC (P-21)	MW 16	25.0	1390	4.20	156
IMC (P21)	MW 17	24.8	1300	4.23	224
Farmland	MW 2	26.0	9100	4.71	177
Farmland	MW 5	25.2	6200	4.68	247
		Feb. 3, 1992			
IMC (P-21)	MW 11	23.0	1380	4.42	39
IMC (P-21)	MW 12	23.3	1920	4.13	93
IMC (P-21)	MW 16	25.0	1380	4.47	111
IMC (P-21)	MW 17	24.0	1420	4.20	212
		Mar. 26, 1992			
IMC (P-21)	MW 11	24.0	1620	4.49	72
IMC (P-21)	MW 12	22.3	1550	4.21	95
IMC (P-21)	MW 16	23.7	1180	4.44	96
		Jun. 16, 1992			
IMC (P-21)	MW 11	24.5	1860	4.92	--
IMC (P-21)	MW 12	23.5	1700	4.18	--
AgriCo	MW 8	26.0	5600	6.40	--

Table 8 (Continued)

Company	Well ID	Temp. °C	Cond. (μmhos)	pH	Sulfide (μM/L)
		Sept. 28, 1992			
IMC (P-21)	MW 11	24.2	2080	4.56	18
IMC (P-21)	MW 12	23.3	1980	4.20	39
IMC (P-21)	MW 16	23.6	1150	4.44	42

Table 9. Radiochemical analysis of groundwaters sampled from monitor wells near gypsum stacks. Errors quoted represent 1σ errors based on counting statistics.

Company	Well ID	^{226}Ra dpm/L	^{222}Rn (pCi/L)	^{210}Pb dpm/L	^{210}Po dpm/L
			Jan. 8-9, 1991		
Farmland	MW 1	2.9±0.2	650± 20	--	14.8±0.1
Farmland	MW 3	13.7±0.3	10100± 150	1.06±0.03	13.1±0.2
Farmland	MW 5	9.9±0.2	6000± 120	--	2.2±0.1
Farmland	MW 6	40.3±0.5	8930± 100	5.68±0.09	12.1±0.2
IMC (P-21)	MW 12	17.6±0.3	61300±2300	4.71±0.07	56.3±0.3
IMC (P-21)	MW 16	30.7±1.2	270± 50	0.58±0.03	3.4±0.1
			Feb. 13-14, 1991		
IMC (P-21)	MW 11	8.7±0.5	5120± 90	--	8.2±0.5
IMC (P-21)	MW 12	20.5±0.3	54900±1700	2.74±0.06	121.2±1.4
IMC (P-21)	MW 16	20.0±0.3	12900± 570	1.10±0.03	17.6±0.2
IMC (P-21)	MW 17	2.8±0.1	4790± 60	1.14±0.13	5.2±0.1
Royster	MW 1	0.6±0.1	2580± 130	--	3.8±0.1
Royster	MW 6	1.1±0.1	36300±1300	0.80±0.04	2.1±0.0
Royster	MW6/2	1.5±0.1	28700± 310	--	
Royster	MW 9	0.9±0.1	7530± 430	--	0.7±0.0
Royster	MW 9/2	--	11700± 80	--	
			March 25-26, 1991		
IMC (P-21)	MW 12	19.1±0.3	68000± 230	--	147.6±1.6
IMC (P-21)	MW 16	40.1±1.0	21200± 250	--	102.6±0.7
CF Industries	SW-1	6.8±0.2	39700± 200	3.5±0.1	1.6±0.1
CF Industries	SW-2	30.8±0.5	1040± 20	618.6±0.5	17.4±0.2
CF Industries	SW-3	67.9±0.6	8900± 100	73.5±0.8	181.1±3.2
CF Industries	SW-5	0.4±0.1	18600± 530	2.4±0.1	1.1±0.1
			April 30, 1991		
Occidental	SC 3S	0.8±0.1	2000± 90	0.15±0.02	2.1±0.2
Occidental	SC 4D	1.3±0.1	2260± 70	0.17±0.05	0.3±0.1
Occidental	SC 4S	4.3±0.3	2060± 50	<0.09	7.3±0.3

Table 9 (Continued)

Company	Well ID	^{226}Ra dpm/L	^{222}Rn (pCi/L)	^{210}Pb dpm/L	^{210}Po dpm/L
		Jun. 3-4, 1991			
IMC (P-21)	MW 11	<0.03	10900± 490	0.48±0.03	3.0±0.1
IMC (P-21)	MW 12	11.1±0.1	58000± 900	2.78±0.20	139.4±1.0
IMC (P-21)	MW 16	27.4±1.2	20300± 170	2.16±0.04	27.6±0.2
IMC (P-21)	MW 17	3.7±0.1	12400± 280	2.07±0.04	144.5±1.2
IMC (P-21)	MW 18	1.1±0.0	3280± 160	0.28±0.03	0.5±0.1
Cargill	MW 1	0.3±0.0	930± 60	<0.10	1.0±0.0
Cargill	MW 3	3.0±0.1	6080± 40	0.16±0.03	1.4±0.1
Cargill	MW 8	0.3±0.0	400± 30	0.66±0.08	3.7±0.2
		Nov. 7-8 , 1991			
IMC (P-21)	MW 12	19.9±2.5	67490± 650	--	145.6 ±1.3
IMC (P-21)	MW 16	32.9±4.1	21860± 240	--	19.0 ±0.1
IMC (P-21)	MW 17	6.5±0.1	13050± 200	--	
Farmland	MW 2	2.0±0.4	5030± 200	--	12.3±0.3
Farmland	MW 5	4.6±0.5	5840± 100	--	6.4±0.1
		Feb. 3, 1992			
IMC (P-21)	MW 11	2.0±0.2	10530± 220	--	6.2±0.2
IMC (P-21)	MW 12	13.1±0.6	69600±1320	--	180.9±1.6
IMC (P-21)	MW 16	12.15±0.59	22620± 300	--	22.1±0.3
IMC (P-21)	MW 17	2.1±0.1	13430± 180	--	132.6±0.9
		Mar. 26, 1992			
IMC (P-21)	MW 11	4.5±0.2	13480± 300	--	2.8±0.2
IMC (P-21)	MW 12	13.9±0.3	67650±1120	--	146.8±1.0
IMC (P-21)	MW 16	23.7±0.4	21250± 140	--	22.7±0.3
		Jun. 16, 1992			
IMC (P-21)	MW 11	4.5±0.2	13360± 250	--	4.5±0.1
IMC (P-21)	MW 12	23.2±0.5	65320±1330	--	157.6±1.1
AgriCo	MW 8	9.2±0.2	9210± 80	--	25.7±0.2

Table 9 (Continued)

Company	Well ID	^{226}Ra dpm/L	^{222}Rn (pCi/L)	^{210}Pb dpm/L	^{210}Po dpm/L
			Sept. 29 1992		
IMC (P-21)	MW 11	7.6±0.3	14990± 930	--	7.9±0.1
IMC (P-21)	MW 12	30.3±0.5	65760± 230	--	156.6±2.2
IMC (P-21)	MW 16	31.3±0.6	21840± 320	--	17.6±0.2

term" and other variations. It is unlikely that there is any significant input of ^{222}Rn into the groundwaters directly from the gypsum stacks since there is no meaningful relationship between components that are thought to be derived from the phosphogypsum, as radium, with the radon contents. Most likely the wells with high radon activities are simply responding to the presence of naturally elevated uranium decay-series isotopes in the underlying phosphate rock. Although some of the radon concentrations are high, none of the values encountered are outside the range we have encountered earlier during investigations of undeveloped mineralized land in Florida (Burnett *et al.*, 1991). Some of the ^{226}Ra values are high enough, however, to be considered outside of the range normally expected for shallow groundwater, even in mineralized areas.

The highest radium values encountered are in some of the wells around the P-21 stack, MW 6 at Farmland, and in two wells (SW 2 and 3) at CF Industries-Bartow. The P-21 stack is not considered typical, however, of the other gypsum stacks in Florida. As the oldest stack, it is severely cracked and does not have an impermeable barrier field placed between the stack and the substrate to prevent migration of contaminated groundwater. The way the mining was carried out in this area, however, left a matrix of impermeable material which functions as an aquitard and constrains most contamination from the stack from percolating directly into the surficial aquifer. The CF Bartow wells that display high ^{226}Ra also have the highest activities of ^{210}Pb and ^{210}Po of all wells sampled in this study. This is undoubtedly related to the unusually high acidity present in these wells during the period when the samples were collected. The extremely low pH values measured in these groundwaters (1.57 and 2.04 - see Table 8) are also atypical, even for groundwaters associated with gypsum stacks, and apparently resulted from contamination of these wells from the nearby cooling ponds.

Fractionation of Radionuclides to Raw Phosphoric Acid

Guimond and Windham (1975), May and Sweeney (1982), and Guimond (1990) presented limited data on Th in phosphoric acid and in phosphogypsum. The two analyses of Th in Florida phosphate rock and phosphoric acid presented the first evidence that most of the Th as well as the U may fractionate to the phosphoric acid. Activities of ^{230}Th and ^{232}Th (^{232}Th is very minor in phosphate ores) in 17 Florida phosphogypsum samples and 11 ore rocks and the approximate percentage of ^{230}Th in the phosphogypsum are given in Tables 5 and 6. These data provide unambiguous evidence that only about 25% of the ^{230}Th reports to the phosphogypsum. This is surprising in light of the extremely surface reactive nature of this element. Gascoyne (1989) mentions the kinetics of Th sorption is so rapid that Th produced by decay of U in natural systems is immediately hydrolyzed and sorbed by the nearest solid. This explains concentrations of $<1x10^{-12}$ mg/L for Th in natural solutions and seawater (Kaufman, 1969), but processing solutions at gypsum stacks are not natural by any description and commonly have pH values less than 2 and very high ionic strengths. No Th analyses have been reported for

processing/cooling waters in these systems, but Th is likely bound to particulates upon release from lattice sites and is probably transported on very fine-grained phases during the preliminary filtering rather than as dissolved species in phosphoric acid.

The ($^{230}Th/^{238}U$) activity ratios in ore rocks and ore slurries in Table 5 average 0.99 and are greater than 0.96 in all but one sample confirming that beneficiation of ores and slurrying ore rocks does not appreciably alter these activity ratios. The same activity ratios in corresponding phosphogypsums are variable and can be much greater than 1, but are generally close to unity, even though a majority of Th is apparently fractionated to the acid. Some ^{230}Th is undoubtedly included in the less soluble or unreacted fraction of the ore rock and may be sorbed preferentially onto clays, but it is not clear what proportions of the nuclides are in lattice sites in resistate minerals, co-precipitated in discrete mineral phases, or are sorbed on fine-grained phases in phosphogypsum. **Figure 1-10,** which is a plot of ($^{230}Th/^{238}U$) versus ($^{234}U/^{238}U$) for the 17 phosphogypsum samples and replicates listed in Table 5, shows a cluster of samples near unity on both axes which represents secular equilibrium of ^{238}U, ^{234}U, and ^{230}Th. Another group of phosphogypsum samples have ($^{234}U/^{238}U$) near 1, but plot below the first group of samples implying loss of ^{230}Th or preferential incorporation of ^{234}U by some phosphogypsum. The four samples in Figure 1-10 that plot far above the equiline with ($^{234}U/^{238}U$) much greater than 1 contain significantly more ^{230}Th and excess ^{234}U. These nuclides are probably sorbed on clays, complexed with phosphate, and perhaps on organic material in the case of ^{234}U. Most phosphogypsum samples we have analyzed seem to have near equilibrium values of ($^{234}Th/^{238}U$) as well as ($^{230}Th/^{238}U$). Activities of ^{234}Th for "fresh" phosphogypsum did not change appreciably when the selected samples were re-analyzed six or more months after the first measurement indicating there was no appreciable excess ^{234}Th.

CONCLUSIONS AND RECOMMENDATIONS

The technique we have developed for determining ^{238}U activities in bulk samples by measuring ^{234}Th via y-ray spectrometry and applying an attenuation correction factor that can be further related directly to packing density has proved to be very successful. Activities of ^{238}U in 29 samples of phosphogypsum and ore rocks analyzed using both gamma and alpha spectrometry compare exceptionally well.

Florida phosphate ore rocks analyzed in this study have ^{238}U activities which range from ~50 - 120 dpm/g for central and southern Florida ores and ~15 to 60 dpm/g for a limited number of ore samples from northern Florida. Activities of ^{238}U decay products are comparable to the uranium activity in ores from each region. These results confirm that the various members of ^{238}U decay chain,

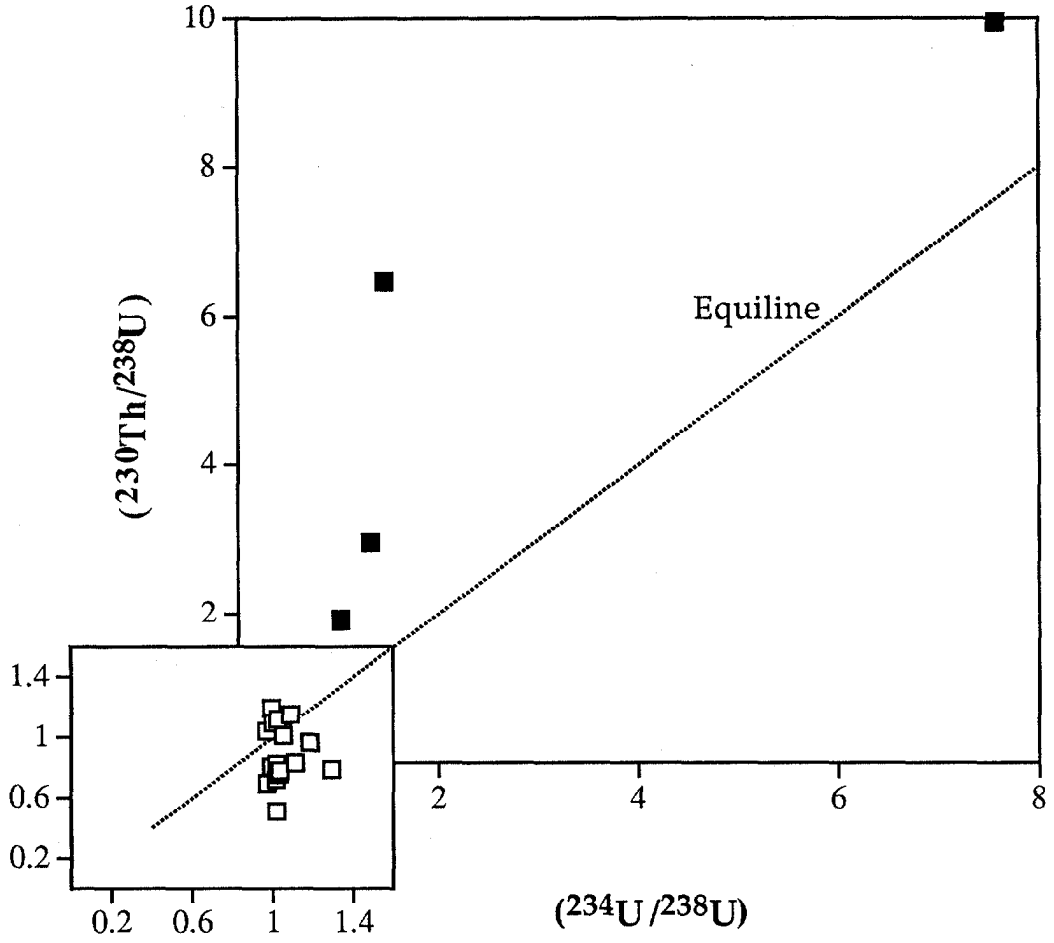

Fig. 1-10 Plot of activity ratios ($^{230}Th/^{238}U$) versus ($^{234}U/^{238}U$) for 17 samples of phosphogypsum. Replicate analyses have been produced and are plotted for most samples. Error bars are smaller than plotting symbols.

including ^{238}U, ^{230}Th, ^{226}Ra, ^{210}Pb, and ^{210}Po, are in approximate radioactive equilibrium in Florida phosphate ores.

During acidulation of Florida phosphate ores, the great majority of ^{226}Ra, typically 90 - 100%, is fractionated to the phosphogypsum and virtually all and occasionally excess amounts of ^{210}Pb and ^{210}Po are present in fresh phosphogypsum. In most cases the activities of ^{226}Ra, ^{210}Pb and, to a lessor extent, ^{210}Po in phosphogypsum are directly and predictably proportional to the activities in the input phosphate rock, indicating that the extent of incorporation of these nuclides into the phosphogypsum is primarily controlled by the amount supplied by the ore rock. Since the activities of ^{210}Pb and ^{210}Po are comparable to ^{226}Ra, even for the majority of fresh phosphogypsum samples, the predominant source of these nuclides is the phosphate rock and not due to ingrowth of decay products during storage. The partitioning of ^{230}Th and ^{238}U between ore rocks and phosphogypsum is more variable. The dissolved uranium is incorporated in the acid phase; however, up to 50 - 60% of U may fractionate to the phosphogypsum and emphasizes that the redistribution of ^{238}U and ^{230}Th during acidulation of phosphate rock is controlled by a number of factors. The ^{238}U activities of Florida phosphogypsums shows no significant correlation to the ^{238}U in the ore rock and may simply be related to the extent of unreacted ore, oversaturation and re-precipitation of calcium fluorapatite in production processes, and sorption and co-precipitation of U with complex Fe phosphates, fluorosilicates, and other phases.

Radionuclides in portions of some Florida phosphogypsum stacks have apparently been mobilized during storage. A few phosphogypsum samples that have been on stacks two or more years have ($^{210}Pb/^{226}Ra$) less than 0.85 so ^{226}Ra must have been added to the sample or ^{210}Pb lost and *vice versa* when ($^{210}Pb/^{226}Ra$) is greater than 1.1. Activity ratios of ($^{210}Pb/^{226}Ra$) less than 0.85 in about 10% of older samples could result from either or a combination of the processes described above or by Pb loss from the sample during storage. Ra is believed to be relatively immobile on the unsaturated, aerobic portions of gypsum stacks in comparison to ^{210}Pb. Isotopic ratios clearly indicate that at least two samples of "mature" phosphogypsum lost Pb during storage. The opposite process seems to be true for a few older phosphogypsum samples. The ($^{210}Pb/^{226}Ra$) and ($^{210}Po/^{210}Pb$) ratios in these samples indicate that ^{210}Pb had been added to the samples from solutions percolating through the gypsum stacks sometime during the two years preceding collection. The processes of Pb leaching, mobilization, and resorption/ precipitation seem to be responsible for most observed ($^{210}Pb/^{210}Po$) disequilibrium. This interpretation is consistent with some of our groundwater data which show occasionally very high ^{210}Pb and high ($^{210}Pb/^{210}Po$) activity ratios. We conclude that ^{210}Pb may be remobilized preferentially to ^{210}Po at surface conditions on gypsum stacks and a net loss of Pb from the stacks by leaching would thus enrich the associated groundwater with ^{210}Pb. Activities of ^{210}Po and ^{210}Pb in process waters

which is being used to slurry fresh phosphogypsum should be measured before attributing any one process or series of processes as responsible for ^{210}Po and/or ^{210}Pb fractionation in fresh phosphogypsum.

There is a wide range of pH, electrical conductivity, and sulfide concentrations in surficial groundwaters collected from monitor wells waters adjacent to phosphogypsum stacks in Florida. There are also appreciable variations in the activities of radioelements in these well waters. Some of the radon concentrations are relatively high, but none of the values encountered in this study are outside the range encountered during earlier investigations of undeveloped mineralized land in Florida (Burnett *et al.*, 1991). Some of the ^{226}Ra values are high enough, however, to be considered outside of the range normally expected for groundwaters in the surficial aquifer systems in this region. The highest radium values encountered so far are adjacent to stacks that do not have an impermeable barrier placed between the stack and the substrate to prevent migration of contaminated groundwater and in wells with water pH less than 2. Wells waters that display high ^{226}Ra also have the highest activities of ^{210}Pb and ^{210}Po as well as the lowest pH values.

The activities of ^{210}Pb, ^{226}Ra, and ^{228}Ra (^{228}Ac) in residues from filter screens used to separate phosphoric acid in an phosphoric acid facility in central Florida contained elevated activities of ^{226}Ra, ^{210}Pb, and ^{210}Po. Barite was positively identified by XRD in a very small sample of scale from the filter screen and this leached scale has the highest specific activity of ^{226}Ra measured during study (>35,000 dpm/g). Although a radiobarite type of phase does apparently exist on these types of screens, barite has yet to be identified in phosphogypsum by XRD and SEM procedures. Further studies intended to delineate the actual sites of radionuclides in phosphogypsum are presented in Chapter 2.

CHAPTER 2

DISTRIBUTION AND MOBILIZATION OF RADIONUCLIDES IN FLORIDA PHOSPHOGYPSUM

INTRODUCTION

One of the major goals of the radiochemistry portion of this study was to characterize bulk samples of Florida phosphogypsum in order to provide a more comprehensive data base of uranium-series nuclides in phosphogypsum than currently exists. These results, presented in **Chapter 1** of this report, constitute the radiochemical foundation required to develop the second major line of the radiochemical research. This research, involves dissolution and leaching of bulk samples of well-characterized Florida phosphogypsum, identifying and assessing radionuclide re-mobilizations during leaching experiments, and developing techniques for isolating and concentrating specific radionuclides from phosphogypsum matrices.

General Research Approach

We have attempted to determine the distribution of radionuclides within Florida phosphogypsum by analyzing not only bulk samples for specific activities of radionuclides, but also in different phosphogypsum fractions, separated by: (i) size fractionation; (ii) sequential leaching of the solid phase material by various chemical reagents; (iii) selective dissolution techniques; and (iv) total dissolution of the gypsum phase.

Chemical partitioning techniques (sequential leaching, selective, and total dissolution approaches) have been used to concentrate insoluble residue fractions from bulk samples of phosphogypsum prior to radiochemical characterization of the insoluble material. Partial dissolution techniques (both single dissolution and

sequential multiple dissolution approaches) have been used to concentrate the radium fraction and other radionuclides from phosphogypsum. Total dissolution of the gypsum phase and separation of the water insoluble residues into density fractions using heavy liquid techniques has also been applied. Analyses of different size, density, and chemically-partitioned fractions, together with examination by X-ray diffraction (XRD), scanning electron microscopy (SEM) were used to identify probable mineral and chemical sites of radionuclides within the phosphogypsum. Solutions produced during dissolution experiments were analyzed for specific activities of ^{226}Ra to determine if radium is mobilized during leaching and to provide additional information on how radium is bound within the phosphogypsum matrix.

Previous Work

The initial work on the location of radium in phosphogypsum was presented by May and Sweeney (1982). They reported that most ^{226}Ra is present in the finest size fraction although only 3 fractions were analyzed (<0.045 mm; 0.045-0.250 mm; and >0.250 mm) in their investigation. In a study of the ^{226}Ra of agricultural gypsum, Lindeken and Coles (1978) reported that during the wet process phosphoric acid production, uranium follows the acid phase, probably as a uranyl sulfate (or phosphate according to Moisset and Lafarge, 1980), while radium coprecipitates with gypsum as $RaSO_4$. No evidence was given in their work that radium actually forms a separate mineral phase. In fact, concentrations of Ra would have be 3 to 4 orders of magnitude higher than the average concentration calculated from activities of ^{226}Ra in Florida phosphogypsum (Chapter 1 of this report) for $RaSO_4$ to precipitate as a discrete phase (Langmuir and Riese, 1985; Upchurch *et al.*, 1991). Therefore, one working hypothesis in our approach to this research is that radium could be incorporated in a (Ra,Ba, Pb)SO_4 solid solution or "mixed" phase in the gypsum or is sorbed on crystal surfaces of the phosphogypsum matrix, or a combination of both.

Prior to this research only the French scientist, J. Moisset, had published findings on the actual site(s) in phosphogypsum that are occupied by radium as an integral part of an approach to find a way to remove radium from bulk samples. He proposed that radium is probably located together with calcium, strontium, and barium sulfate in small crystals of 4-8 μm in diameter (Moisset, 1988). However, a mineral phase with this composition would be very unstable because the Gibbs free energy of the crystal would be negative. Another population of even smaller (about 1 μm diameter) crystals of unidentified composition were also tentatively identified as containing significant amounts of radium. However, Moisset's results must be considered tentative because of the inability to directly detect radium via the secondary electron emission analyzer used in that study.

Moisset and Lafarge (1980) had earlier proposed a hydrocycloning treatment process to remove radium from phosphogypsum. Unfortunately, this process proved to be unable to eliminate the radium located in the smallest-sized crystals (1 μm size) which apparently stick to the surfaces of the larger calcium sulfate crystal. Recently,

Moisset suggested a process which can be used to obtain purified phosphogypsum of a better quality, free of radium and other non-soluble impurities (Moisset, 1990). In this new approach, raw phosphogypsum is calcined into hemihydrate to increase its solubility and then dissolved in water with a water/phosphogypsum ratio greater than 100 : 1. Radium and other impurities which are included in the less soluble, fine-grained fraction are left behind and then filtered off. The filtrate is a purified solution of calcium sulfate which can then be recrystallized into gypsum that is relatively free of the radium impurities. We have analyzed samples of "purified" phosphogypsum that were provided by J. Moisset and found the "purified" samples were also low in ^{210}Pb and ^{210}Po. However, this process may not be efficient on an industrial scale because of the expense of calcining large quantities of phosphogypsum.

Published research on the site(s) of radionuclides in phosphogypsum is otherwise limited. There is some evidence that a portion of the ^{226}Ra may be associated with radiobarite types of mineral phases on filter screens and pans in phosphoric acid plants. Activities of ^{226}Ra (up to 220,000 dpm/g) are found in the small quantities of scale associated with the filter pan which separates gypsum from the phosphoric acid (Keaton, 1987; this study). Kraemer and Curwick (1991) reported fluxes of radium isotopes both upstream and downstream of a phosphoric acid plant that was discharging phosphogypsum directly into the Mississippi River. They presented ratios of adsorbed (on suspended sediment)/dissolved ^{226}Ra at three sites downstream of the phosphogypsum discharge that were 1.04, 1.32, and 1.04. The ratio in the mixing zone immediately downstream of the discharge plume was only 0.19 which implies that about 80% of the ^{226}Ra was in solution even though the concentration of suspended sediments was higher at this point that at any other sampling locality. Recent work by Rutherford *et al.*, (in press) have addressed the mobilization of ^{226}Ra as phosphogypsum is leached with deionized water and a strong correlation between Ba and Ra was shown in residues and leachates. Conclusions drawn from this work are that radium is associated with Ba and is likely coprecipitated with Ba in sulfate phases. Very small (a few microns in diameter) radium-enriched particles, also enriched in Pb and Ba, have been identified in a sample of phosphogypsum using the X-ray diffraction unit at the State of Florida Institute of Phosphate Research (FIPR) (H. El-Shall and M. Bogan, pers. comm.).

Objectives of the Research

The primary objectives of this research were to characterize how radium and other radionuclides in phosphogypsum are sited and bound within the matrix of the by-product material. The first priority was to determine whether radionuclides are distributed uniformly throughout phosphogypsum, if they are incorporated in a separate mineral phase(s), or sorbed or exchanged on mineral surfaces in the matrix. Our reasoning rested on the assumption that locating the sites and bonding characteristics of radionuclides within phosphogypsum was a first step toward the ultimate goal of developing techniques to remove the majority of radionuclides from

phosphogypsum. In this manner, a waste material could conceivably be transformed into a useful product.

EXPERIMENTAL PROCEDURES

Procedures for analyzing the specific activities of radionuclides in bulk samples of ore rocks, phosphogypsum, solid residues, monitor well waters, and miscellaneous samples such as filter screens were presented in Chapter 1 of this report and are not reiterated here. Analytical procedures for physical and chemical fractionation of selected samples of phosphogypsum, preparing solid fractions for radiochemical analyses, analyzing solid fractions for chemical compositions, and procedures for preparing supernatant solutions produced in leaching experiments for radiochemical analyzes are presented below.

Size Fractionation Studies

Selected bulk phosphogypsum samples have been physically disaggregated to analyze radionuclide activities in the discrete size fractions to evaluate if the radioelement-rich component can be mechanically segregated into one or a few size classes. Approximately 100 grams of vacuum dried sample was preweighed before dry-sieving. The sample was separated into standard size divisions by ultrasonic techniques through the following series of 1φ interval screens: >2,000 μm (-1φ); 1,000-2,000 μm (0φ); 500-1,000 μm (+1φ); 250-500 μm (+2φ); 125-250 μm (+3φ); 62.5-125 μm (+4φ); and <62.5 μm (+5φ). After size separation, all size fractions were weighed and size distributions calculated. The sample loss during the dry-sieving and the distribution of particle sizes were calculated by considering the weight of the individual size fractions and the initial weight used for dry-sieving. Individual fractions were then dried, ground, and analyzed for radionuclides by γ-spectrometry.

Sequential Leaching Experiments

A series of sequential leaching solutions were used which had previously been proved to be useful in the identification of the phases hosting radium in soil (Greeman et al., 1990). The solutions used in the sequence consisted of: (i) doubly deionized water, DDW; (ii) a 3% NaCl solution; (iii) 5% sodium hypochlorite or "bleach", NaOCl; and (iv) a 0.25 M solution of the chelating agent Ethylenedinitrilo-tetraacetic acid disodium salt, EDTA. Sequential leaching was carried out by using an accurately weighed, approximately 5.5 gram portion of each phosphogypsum sample (dried and ground), divided into two 50 mL centrifuge tubes. Fifteen mL of reagent were added to each tube, the sample was agitated in an ultrasound bath for 5 minutes, and then heated in a hot water bath for another 5 minutes. After two cycles of agitation and heating were performed, the sample was centrifuged at 2500 rpm for 10 minutes. Two cycles with each reagent and one with DDW were performed in every case. All three supernatant solutions for each sequential step were then combined for ^{226}Ra analysis by

the ^{222}Rn emanation method. The solid residues were dried and ground for solid phase radionuclide analysis by gamma spectrometry.

Selective Solubility Experiments

Phosphogypsum samples used for selective dissolution in EDTA were dried either in an air/desiccator at room temperature (dihydrate gypsum, DH) in a temperature-controlled oven at 55°C or 120° C (predominantly hemihydrate, HH), or in a furnace at 600° C (anhydrite). Different temperatures were used so that mineralogical effects on solubility and release of radium and other radionuclides could be evaluated. Sample powders were mineralogically characterized by X-ray diffraction procedures. All samples were ground with a mortar and pestle, dried as described above, and thoroughly homogenized before dissolution. Accurately weighed portions of approximately 4.4 grams of homogenized samples were placed in either a 125 mL or 500 mL Erlenmeyer bubbler flask for each run. The flask was then placed on an automatic shaker table, and samples were allowed to react with varying volumes of EDTA (these volumes ranged from 50-250 mL) for measured time intervals of 45 hours. Samples were allowed to settle, and then centrifuged at 2500 rpm for 10 minutes and decanted. The remaining residue was washed with 10 mL DDW two times, and the three supernatant solutions were combined and transferred to an Erlenmeyer flask for radon emanation analysis. The residue was dried to constant weight and prepared for radiochemical analysis. Solubility calculations were based on the final weight of the dried residue normalized to the sample weight initially present. We determined the time required for phosphogypsum dissolution in EDTA by setting up a similar experiment with replicate samples run for different time periods. Approximately 2.2 grams of dried, ground, and accurately weighed sample was used for each replicate, and samples were allowed to react with 25 mL EDTA for times varying from about 0.5 - 1,500 minutes.

Other experiments were conducted using DDW and dilute HCl solutions under similar conditions. Both calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$) and calcium sulfate hemihydrate ($CaSO_4 \cdot 1/2H_2O$) are produced in the phosphoric acid manufacturing process. DH is by far the predominant by-product produced and stored in Florida. Samples of both air-dried DH and HH dried at 160°C were used in these experiments. In order to assess possible binding of radionuclides by organic matter (this has been shown by Greeman *et al.*, 1990, as being important for radium in soils), experiments were conducted with and without addition of 30% H_2O_2 (Schmiermund, 1977). For the H_2O_2 pre-treated experiments, about 4.5 grams of sample was put in a 50 mL centrifuge tube and 25 mL of hydrogen peroxide was added, stirred and left overnight. The next day, the tube was heated in the water bath until effervescence ceased (about 1 hour). The tube contents were then washed into an empty 3.5-liter Winchester bottle. The volume was brought up to two liters with water or dilute HCl and the bottle was periodically shaken until the undissolved residue appeared to be a constant amount (this required about 5 hours). The bottle then stood overnight and the supernatant decanted, with the last few hundred milliliters being centrifuged or filtered through a

47-mm diameter 0.45μm membrane filter. The solid residue was dried, weighed, and prepared for radiochemical analysis. The procedure for experiments without H_2O_2 pretreatment was essentially the same but the sample was added directly to the Winchester bottle with the reagent.

Radium Adsorption Experiments

In each tracer experiment, 2129 dpm of a NIST ^{226}Ra solution standard was added before sample dissolution. About 4.4 grams of Gyp-6 (25°C) was then reacted with varying volumes of EDTA (0.25M, pH=10). Samples were allowed to react with EDTA for 5 hours, and then the leaching solution was separated by centrifugation, and radium was determined by the radon emanation method. The adsorption experiment was repeated with the same EDTA volume (50 mL) but different pH levels. A blank experiment (no gypsum added) was also performed to test for radium recovery when no adsorption onto gypsum was possible. The residues from these experiments were then analyzed by XRD to determine if any undissolved or DH or HH remained or was reprecipitated.

Radium sorption in DDW solutions were also conducted for replicate samples of Gyp-6 (DH) and Gyp-6 (HH). Two liters of DDW, 1 mL of NIST ^{226}Ra tracer (2129 dpm/mL), and 0.5 mL 2.5N NaOH were added to 3.5-liter Winchester bottles. The bottles were shaken for about one minute and allowed to stand for one hour or so. An accurately weighed sample was added, and the pH was adjusted to 6-7 with 2.5N NaOH. The bottle was then placed on the shaker table for 5 hours and allowed to settle overnight. The supernatant was siphoned and centrifuged, and finally filtered through 47-mm Whatman™ and 0.10 μm pore size polypropylene filters. The filtered solutions were retained in 4-L bottles for analyses of ^{226}Ra by radon emanation. In order to obtain 100% dissolution, one extra liter of DDW was added to dissolve any remaining $CaSO_4 \cdot nH_2O$ for the first 4 experiments. The decanted and centrifuged solutions were filtered as before and added to the same collection bottles for determination of ^{226}Ra tracer recoveries by radon emanation. The residue was then dried in a oven at about 40°C, and prepared for radiochemical and XRD analysis.

Water Insoluble Residues and Supernatant Solutions

"R" Series Dissolution Experiments

The first large quantities of insoluble residues of phosphogypsum samples Gyp-2, Gyp-9, Gyp DL3, and Gyp-46 were produced by dissolving fifty grams of air-dried, homogenized samples in 18 L of DDW in an acid-cleaned 22-L glass bottle. Each 22-L bottle was immediately placed on a custom-built drum rotator and kept turning for two or more days. This set of dissolution experiments is referred to as the “R” dissolution series. Although dilute sodium salt solutions are known to increase the solubility of gypsum (Nakayama, 1971), Na salts were not added to these solutions because some residues were to be analyzed for chemical compositions. After two or more days the 22-

L bottle was removed from the drum rotator and the solid particulate matter was allowed to settle for at least three days to allow the extremely fine-grained material in the suspended load to settle.

The supernatant solution was then siphoned off and discarded. At least 3 L of solution was left above the residue during each dissolution cycle to minimize disturbance of the very fine-grained residue at the solid-liquid interface during the siphoning process. Another 50 g of phosphogypsum was then added to the bottle, about 15 L of DDW were added to make up the total volume to 18.0 L and the entire process was repeated until at least 400 g of bulk sample had been added to each bottle. The process was then repeated with two 18 L rinses of deionized water and one 18 L rinse of doubly deionized water in each bottle without adding phosphogypsum to assure that very little, if any, $CaSO_4 \cdot nH_2O$ remained in the solid residues. Five 22-L bottles were used to produce insoluble residues RES 1 to RES 5 in the Gyp-46 "R" series. All of the residues were analyzed by X-ray diffraction (XRD) which confirmed that almost all $CaSO_4 \cdot 2H_2O$ had been dissolved in these samples. Three 2-L aliquots of the supernatant solutions were siphoned from the 22-L bottles, filtered to 0.22 µm and transferred to acid-cleaned 4-L-bottles for Rn emanation analyses. Three 2-L unfiltered aliquots were similarly processed. Analyzes for ^{226}Ra in solution were performed using the Rn emanation technique.

"RAS" Series Dissolution Experiment

A 50 g sample of air-dried, homogenized Gyp-46 was added to 18.0 L of DDW in an acid-cleaned 22-L bottle. The bottle was rotated on the drum rotator for 3 days and was then allowed to stand undisturbed for 9 days. Four filtered and 3 unfiltered 2 L aliquots of the supernatant solution were carefully removed from about 10 cm above the sediment-solution interface using a peristaltic pump. Filtered solutions were pumped through either a 0.22 µm or 0.45 µm filter in an in-line filter holder into an acid-cleaned graduated cylinder and then decanted into acid-cleaned 4 L-bottles for analyses of ^{226}Ra in solution by Rn emanation. This dissolution experiment is referred to as the "RAS" dissolution.

"D" Series Dissolution Experiments

A variant of the "RAS" series dissolution process was used to dissolve the water soluble fractions of additional lots of homogenized samples of Gyp-46, Gyp DL3, and Gyp-6. About 25 g of dry and homogenized phosphogypsum was added to 18-L of DDW in a glass bottle that was sealed and then kept rotating constantly for several days. Six water insoluble residues of Gyp-46, 5 samples of residues of Gyp DL3, and 3 insoluble residues of Gyp-6 were produced using this technique. After removing the bottle from the rotator, the residues were allowed to settle for a few minutes and the supernatant solutions which contained virtually all of the finer-grained, suspended material (SM) was quickly transferred to a second acid-cleaned, 22-L glass bottle using a peristaltic pump. The solids that settled out in the first 22L bottle were rinsed twice

with DDW, the coarser-grained sediment allowed to settle for 2 or 3 minutes, and these solutions were combined with those in the bottle containing the SM. The granular, coarser-grained residues (called "Solids") were then transferred to an acid cleaned, 500 mL beaker and allowed to settle for one or two days or until the supernatant solution was clear and it was siphoned off and combined with the SM supernatant solution. The 22-L bottles containing the SM samples were not moved or agitated for at least one week after rotation to allow the extremely fine-grained material to settle out of solution. One insoluble residue of each bulk. phosphogypsum sample in the "D" series dissolution experiments was not fractionated by grain size and the total insoluble residue was dried and homogenized. Three filtered and unfiltered aliquots of supernatant solutions from each bottle were carefully pumped across 0.22 µm or 0.45 µm filters in an in-line filter holder using a peristaltic pump into an acid-cleaned graduated cylinder and then decanted into acid-cleaned 4-L bottles for analyses of ^{226}Ra in solution by Rn emanation. The 25-g samples dissolved in this way are referred to as the "D" series dissolution experiments.

The water insoluble residues of "D" series dissolutions that were separated by the suspension technique into two fractions, the coarser-grained sediments comprised mostly of quartz sand (Solids) and suspended material (SM). These fractions were processed separately. The two fractions were dried, homogenized, and prepared for radiochemical analyses. Selected samples were also prepared for compositional, XRD, SEM, and organic carbon analyses. Activities of radioactivities in the total residues and in the coarse- and fine-grained fractions were measured to determine whether radioactivities and masses were balanced and internally consistent.

"SD" Series of Dissolution Experiments

The fourth dissolution process used smaller masses of about 2.8 g of homogenized phosphogypsum samples which were dissolved in 2-L of DDW in 3.5-L Winchester bottles. Winchester bottles were then agitated on a shaker table for 8 or more hours. The solutions were allowed to settle for several days and then the supernatant solutions were filtered through 0.45 µm polypropylene filters. One liter of the supernatant solutions were transferred to acid-cleaned, 4-L bottles for Rn emanation analyses. The 1.0 L solutions in the Rn bottles were brought up to a total volume of 2.0 L by adding a liter of DDW and the solution pH was lowered to less than 2 by adding 15 to 20 mL of nitric acid. These solutions were then prepared for radon emanation analyses for determining ^{226}Ra in solution. These smaller dissolution experiments are referred to in subsequent sections as the "SD" series of dissolution experiments.

Identification of Solids

X-ray Diffraction

XRD patterns have been produced for bulk samples of phosphogypsum and many leached residues and size fractions of residues. Samples were powered and analyzed *via* a Philips vertical goniometer X-ray diffraction unit with a computerized APD 3520

Control Console and an XRG-2500 Generator at the Department of Geology at Florida State University. Selected samples of solids on filters were analyzed by XRD at FIPR using the automated peak search software and the FIPR and Tennessee Valley Authority XRD databases for phosphogypsum, phosphate rocks, and phosphatic clay phases.

Scanning Electron Microscopy/Energy Dispersive X-ray Analysis

We have utilized two SEM units, the JOEL 840A Scanning Electron Microscope (SEM) at the Institute for Materials Research and Technology at Florida State University and the JOEL 840 SEM in the Department of Biological Sciences at Florida State University. Both instruments are equipped with energy dispersive X-ray analyzers. Most samples were mounted on aluminum plugs and coated with graphite. Samples for imaging studies were mounted on aluminum discs and coated with a microlayer of a gold/palladium alloy. Duplicate SEM mounts of phosphogypsum residues were analyzed for Ba, Sr, Pb, and S in the finest-grained, water insoluble residues of Gyp-2. Replicate samples of the finest-grained, water-insoluble, suspended material in Gyp-6 Gyp DL3, and Gyp-46 were collected on 0.10 μm filters and mounted for analysis by SEM imagery and semiquantitative compositional analyses of the elements listed above by energy dispersive X-ray fluorescence (XRF).

Compositional Analyses

Chemical compositions of replicate samples of phosphogypsum, leached phosphogypsum, and water insoluble residues of bulk phosphogypsum samples of Gyp DL3 and Gyp-46 were performed at the Earth Sciences Laboratory at the University of Utah Research Institute in Salt Lake City. Cations were analyzed by inductively coupled mass spectrometry (ICP) and anion and complex ions analyzed by standard techniques including titration, turbidity, and ion specific electrode methods. The samples designated FSU 1 to FSU 6 were produced by dissolving varying proportion of the gypsum fraction of Gyp DL3. Samples RES 1-5 are the water insoluble residues produced during the "R" series of dissolutions of five bulk samples of Gyp-46. Sample RES 6 is a replicate sample of RES 3. Samples RES 7, 8, and 9 are the water insoluble residues of homogenized, bulk samples of Gyp DL3. Samples RES 8 and RES 9 consist of the total water-insoluble residue and RES 7 represents the finest - grained fraction of the water insoluble residue of Gyp DL3 that was separated by centrifugation. The compositional sample designated Gyp-46 is the anhydrous chemical composition of the homogenized bulk sample. Splits of each of these samples were also packed in plastic vials and analyzed for radionuclides by γ-spectrometry. Compositional analyses are listed in **Appendix C.**

Carbon in Residues and Dissolved Organic Carbon

Three replicate pairs of samples of the finest-grained insoluble residue which remained suspended in supernatant solutions of Gyp-46 D3 were quantitatively

analyzed for total organic carbon (TOC) and nitrogen (N) on instrumentation in the Biology Department at Florida State University. Analyses of dissolved organic carbon (DOC) were analyzed in aliquots of supernatant solutions above insoluble residues of 8 Florida phosphogypsum samples at the Marine Environmental Sciences Consortium Laboratory at Dauphin Island, Alabama.

PERALS Analysis of Ra-226 in Solution

Activities of ^{226}Ra in solution were determined for a limited number of samples by PERALS (Photon Electron Rejecting Alpha Liquid Scintillation) spectrometry. PERALS spectrometry combines electronic pulse-shape discrimination (PSD) with the optimization of the detector design and associated electronics for alpha pulses, and use of a liquid-liquid extractive scintillator. Transfer of the alpha-emitting nuclide to a water-immiscible scintillator of constant composition has eliminated many quenching problems and pulse shape discrimination lowers backgrounds by rejecting beta and gamma pulses with a 99.7+% efficiency. The extractant / scintillator solution used for measuring radium in solution in this study was RADEX™ which selectively extracts ionic radium from solution. Although peak resolutions are not as good as with conventional surface barrier and ion implanted silicon detectors used in alpha spectrometry, energy resolution is substantially improved over standard LSC equipment. These improvements allow for energy resolutions that are generally less than 250 keV and a minimum limit of detection of less than 0.01 counts per minute (McDowell and McDowell, 1993).

Heavy Liquid Separations of Insoluble Residues

The major impediment to identifying phase(s) in water insoluble residues that contain radionuclides is that quartz and other common minerals comprise the great majority of the residue. If the radionuclide-bearing material can be separated from the majority of the quartz by mechanical means, the capability to identify the phase(s) by SEM or other techniques would be enhanced. Mixtures of heavy liquids have been used to separate fractions of the water-insoluble residue of Gyp-46 by density to determine whether a radionuclide-enriched fraction could be produced and the mineral phases identified by SEM. The heavy liquids bromoform and xylene were combined in varying proportions to produce numerous liquids each having a discrete range of density. Once a heavy liquid with the desired range of specific gravity was obtained, a homogenous sample of insoluble residue of known mass was wetted with a few drops of the liquid in a clean mortar and pestle. The remainder of the heavy liquid was added, the residue dispersed by stirring and slight grinding to a uniform consistency, and the mixture transferred to a tared centrifuge tube. The residue and heavy liquid mixture in the centrifuge tube were placed in an ultrasonic bath for about 30 seconds and then centrifuged for 4 - 6 minutes. Solids within the density range of the solution remain suspended in the heavy liquid while those with greater densities collect at the bottom of the tube.

The heavy liquid - solid supernatant mixtures were decanted into an extraction tube and filtered with a tared 0.22 μm pore-size polypropylene filters that are resistant to the chemical reagents. The solids in the centrifuge tube were returned to the mortar and pestle and the process repeated with the next density range solution. The tared filters and solids were dried, the masses measured, and the solids carefully removed from the filters and the masses measured again. The solids removed from filters were transferred to plastic vials and the activities of radionuclides measured in the well-type IG y-ray detector after secular equilibrium had been attained. The solids that were denser than the liquid used for that fraction were rinsed with acetone and the supernatants were decanted into a holding beaker. The solid residues were dried, the mass recorded, and the entire process was repeated for each density range of interest.

Theoretical Equilibrium Calculations (SOLVEQ - CHILLER)

Many multicomponent chemical equilibrium models have been developed utilizing software which employs chemical thermodynamic calculations to calculate phase equilibria and reaction paths in closed chemical systems. We used the models of Reed (Reed, 1982; Reed and Spycher, 1984) for calculating homogenous (SOLVEQ) and heterogeneous (CHILLER) chemical equilibria. These models have proven to be very useful for determining solubilities of mineral phases which could conceivably contain ^{226}Ra for a number of solvents under a variety of physiochemical conditions. The usefulness of phosphogypsum dissolution experiments was evaluated using the numerical modeling technique before performing time consuming experiments. Chemical parameters were varied in the model to identify the most advantageous conditions for specific dissolution objectives.

RESULTS AND DISCUSSION

Size Fractionation

Results of dry-sieving were ambiguous with a minor trend of higher activities of ^{226}Ra in the in the fine-grained size classes (**Table 2-1**). Apparently, the dry sieving was unable to completely disassociate aggregate grains. SEM imaging clearly demonstrated that much of the material remaining on each screen size was composed of composite grains of finer-sized particles. When the activities of radionuclides were displayed as a function of size, the distribution of specific activities were relatively "flat", i.e., there was no systematic tendency for concentration of ^{226}Ra or ^{210}Pb activities in any size class. Even after wet sieving, SEM images showed that much of the material remaining on the smallest mesh screen (62.5 μm mesh size) was still composed of aggregate grains of finer-sized particles. These observations are consistent with those discussed by Moisset and Lafarge (1980) who attempted separating the radium-rich fraction from phosphogypsum by hydrocycloning. The only conclusion that can be drawn from these size fractionation studies is that on a laboratory scale neither standard dry nor wet sieving techniques appear to be a viable approach for separating the radionuclide-rich

Table 2-1. Size distributions based on dry-sieving techniques together with radiochemical results for different size fractions from phosphogypsum samples Gyp-4, Gyp-5/1, and Gyp-6. Errors reported for radiochemical results are 1σ based on counting statistics.

Screen Diameter (μm)	Mass Fraction (g)	% Mass (Normalized)	^{226}Ra dpm/g	^{210}Pb dpm/g
		Farmland (Gyp-4)		
>2000	7.61	7.42	77.9±0.8	68±1
1000-2000	8.80	8.58	89.6±0.9	73±1
500-1000	6.11	5.95	89.3±0.9	83±2
250-500	14.97	14.59	71±2	72±4
125-250	22.91	22.33	61±2	64±4
62.5-125	26.59	25.91	64±2	60±4
<62.5	15.63	15.23	70±2	67±4
total =	102.60	100.00		
initial wt =	102.78			
		IMC P-21 (Gyp-5/1)		
>2000	1.19	1.20	85±3	66±6
1000-2000	3.37	3.41	93±2	57±4
500-1000	5.18	5.24	97±2	86±4
250-500	10.61	10.74	68±2	99±4
125-250	21.84	22.11	53±2	69±4
62.5-125	27.30	27.63	55±1	53±2
<62.5	29.30	29.66	69±2	59±5
total =	98.79	100.00		
initial wt =	99.65			
		Royster (Gyp-6)		
>2000	3.53	3.30	70±2	60±4
1000-2000	6.16	5.76	72±2	66±4
500-1000	11.28	10.55	67±2	82±4
250-500	26.11	24.41	47±1	55±3
125-250	26.37	24.66	43±1	37±3
62.5-125	22.73	21.25	52±2	40±3
<62.5	10.77	10.07	62±1	46±2
total =	106.95	100.00		
initial wt	107.34			

fraction of these materials. However, it may be worth investigating more sophisticated sieving techniques which utilize surfactants and/or ultrasonic vibration during the processing and filtering of the solids.

Sequential Leaching Experiments

The initial chemical fractionation experiments were series of sequential leaching solutions that are progressively more vigorous and are "selective" for different fractions (Chao, 1984). The solutions and solid residues are then analyzed for elements of interest. In this way it is possible that an "operationally-defined" fraction may be identified which contains the majority of the radionuclides. Unfortunately, none of the solutions produced in the sequential leaching experiments of Gyp-6 and Gyp-5/1 had elevated activities of ^{226}Ra (**Table 2-2**). When the samples from the first experiment were dried and reweighed at the end of the experiment, it was found that a radiochemically-depleted fraction of the phosphogypsum had been selectively removed, *i.e.,* several times more sample mass was removed by dissolution of the gypsum than the amount of radium liberated so ^{226}Ra was effectively enriched in the solid residue. However, the $CaSO_4 \cdot nH_2O$ had not been completely dissolved in these experiments. This may have an important effect on the interpretation of these results as will be discussed in a later section.

Selective Solubility Experiments

Results of the selective solubility experiments of two phosphogypsum samples in solutions of 0.25 M EDTA are shown in **Table 2-3**. When the percentage of the sample that is dissolved is plotted versus EDTA volume for an air-dried sample, the percent dissolved curve goes up rapidly at first as the EDTA volume increases, and then the slope becomes horizontal **(Figure 2-1**). Above this point, about 5% insoluble sample still exists even though the EDTA is in excess at these higher volumes. This represents the EDTA insoluble fraction of the gypsum, containing insoluble residues such as SiO_2, clays, minor phases such as complex iron and aluminum phosphates, organic matter, *etc.*, and perhaps other sulfate mineral phases. Results of the dissolution time experiment **(Figure 2-2**) shows that phosphogypsum dissolves very quickly in EDTA. The solution quickly reaches a lower solubility condition in less than 1 minute and then rises to the theoretical solubility (about 40 g/liter) after about one hour. However, the dissolution time curve showed an unexpected feature later in the experiment. After the initial rise to a solubility plateau which persists for about 8 hours, the solubility suddenly decreased. A possible explanation for this phenomenon is that the solution is supersaturated with a relatively less soluble mineral phase(s) during this time period because of the vigorous agitation on the shaker table, and the phase(s) precipitates as chemical equilibrium conditions are approached and the solution adjusts to the stable, lower level of solubility for radium in this system.

When ^{226}Ra in solution (given as a percent of the total) is plotted versus the weight percent of sample dissolved **(Figure 2-3**) it is clear that ^{226}Ra does not enter solution

Table 2-2. Results of sequential leaching of phosphogypsum samples Gyp-5/1 and Gyp-6 by various reagents. The Sample/Radium ratio given in this table represents the percent of sample dissolved divided by the percent of the ^{226}Ra leached from the sample. Note that gypsum in these samples was not completely dissolved.

Reagent	Ra Activity (dpm)	Ra Leached (%)	Dissolved (grams)	Dissolved (%)	Sample/Radium Ratio
			Gyp-6		
DDW	5.31	1.91	--	--	--
NaCl (3%)	10.82	3.89	--	--	--
NaClO (5%)	9.24	3.32	--	--	--
EDTA (0.25 M)	10.11	3.63	--	--	--
Total	35.48	12.75	3.08	54.12	4.2
			Gyp-5/1		
DDW	10.47	3.69	0.02	0.27	0.1
NaCl (3%)	11.97	4.22	0.50	8.77	2.1
NaClO (5%)	16.72	5.89	0.93	16.34	2.8
EDTA (0.25 M)	37.34	13.16	2.31	40.52	3.1
Total	76.50	26.96	3.76	65.90	2.4

Gyp-6	Initial wt = 5.6842 (g)	Initial Ra = 49.0 dpm/g	Final Ra = 81.6 dpm/g
Gyp-5/1	Initial wt = 5.7078 (g)	Initial Ra = 49.7 dpm/g	Final Ra = 99.6 dpm/g

Table 2-3. Results of selective leaching experiments of two phosphogypsum samples of constant weight (Gyp-4 and Gyp-6) with varying amounts of 0.25 M EDTA after different drying temperatures and at different pH values.

EDTA (ml)	Solubility (g/l)	Dissolution (%)	EDTA-Ra (dpm)	EDTA-Ra (%)
		Gyp-6 (25°C, pH=10)		
50	38.8	44.1	30.3	14.1
75	36.9	62.8	26.6	12.4
100	36.7	83.4	52.8	24.5
125	33.2	94.0	98.9	45.9
175	24.0	95.4	159.0	73.6
250	16.8	95.1	101.0	47.9
		Gyp-6 (55°C), pH=10)		
50	34.5	39.2	26.5	12.3
75	39.4	67.2	29.2	13.5
100	37.5	85.1	31.3	14.5
125	33.4	94.9	75.0	34.8
		Gyp-6 (120°C, pH=10)		
50	19.4	21.9	29.6	13.8
75	33.5	57.1	13.5	6.2
100	32.8	74.6	31.1	14.4
125	31.0	88.2	63.0	29.2
		Gyp-6 (600°C, pH=10)		
50	32.5	36.9	9.3	4.3
75	32.0	54.5	7.8	3.6
100	31.8	72.1	8.7	4.0
125	29.8	84.6	28.0	13.0

Table 2-3 (Continued)

EDTA (ml)	Solubility (g/l)	Dissolution (%)	EDTA-Ra (dpm)	EDTA-Ra (%)
		Gyp-4 (25°C, pH=10)		
50	43.2	49.0	17.6	6.0
75	42.4	72.2	26.1	8.9
100	37.9	85.9	49.6	17.0
125	30.8	87.4	161	55.2
Temp		*Gyp-6 (50 ml EDTA, pH=6)*		
25°C	9.7	11.0	15.9	7.4
55°C	5.6	6.4	12.5	5.8
120°C	-*	-*	9.4	4.4
600°C	16.3	18.5	16.3	7.6

* Sample gained mass, apparently by hydration.

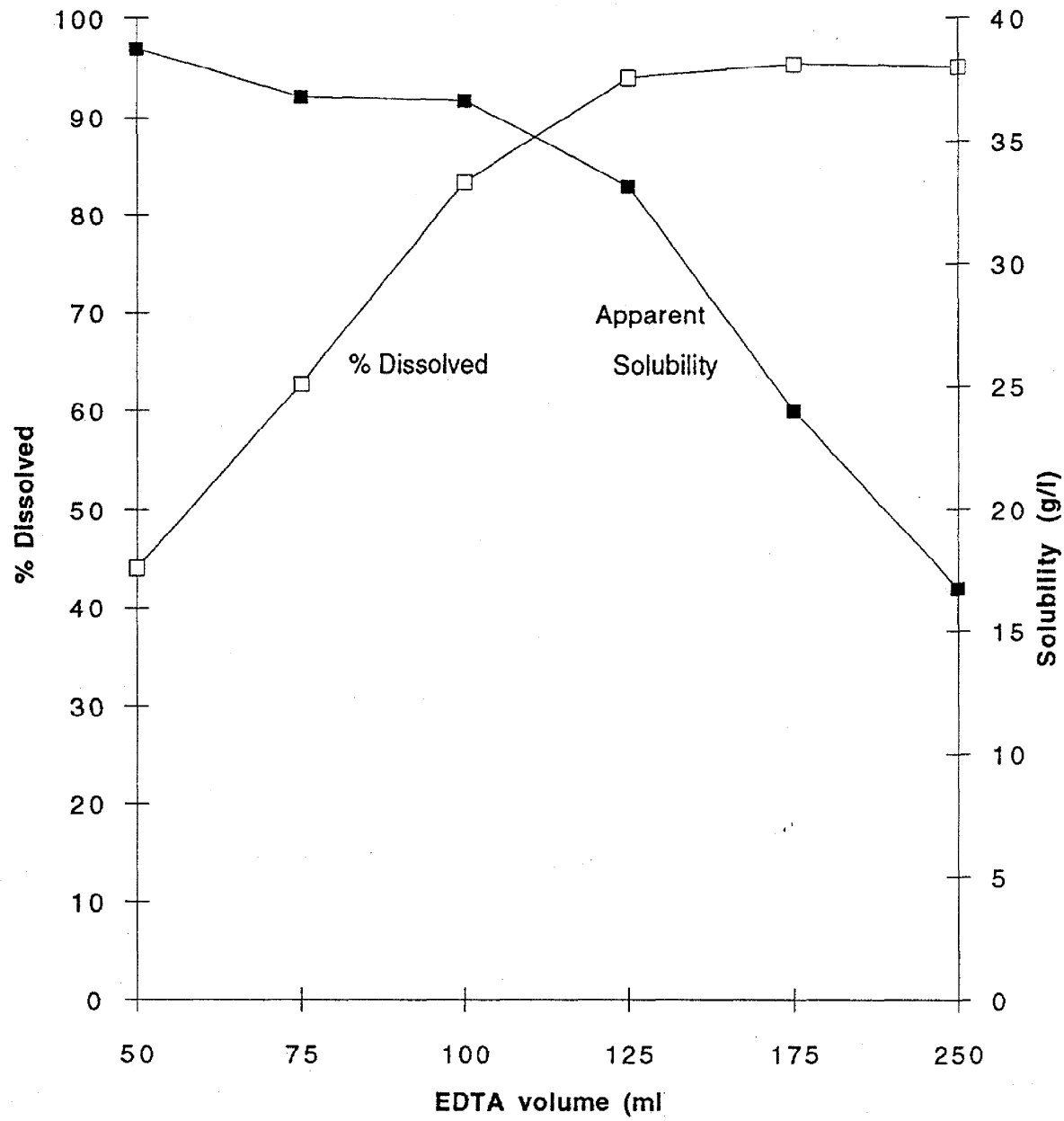

Figure 2-1. Fraction of constant weight (4.4 grams) of phosphogypsum sample Gyp-6 dissolved *versus* volume of 0.25 M EDTA at pH=10 added (left-hand scale). The apparent solubility of the phosphogypsum (right-hand scale) appears to decrease with increasing volume because the EDTA dissolves the more soluble fraction ($CaSO_4 \cdot n\ H_2O$) until totally depleted and then attacks the less soluble fractions of the solid which may contain other sulfate mineral phases.

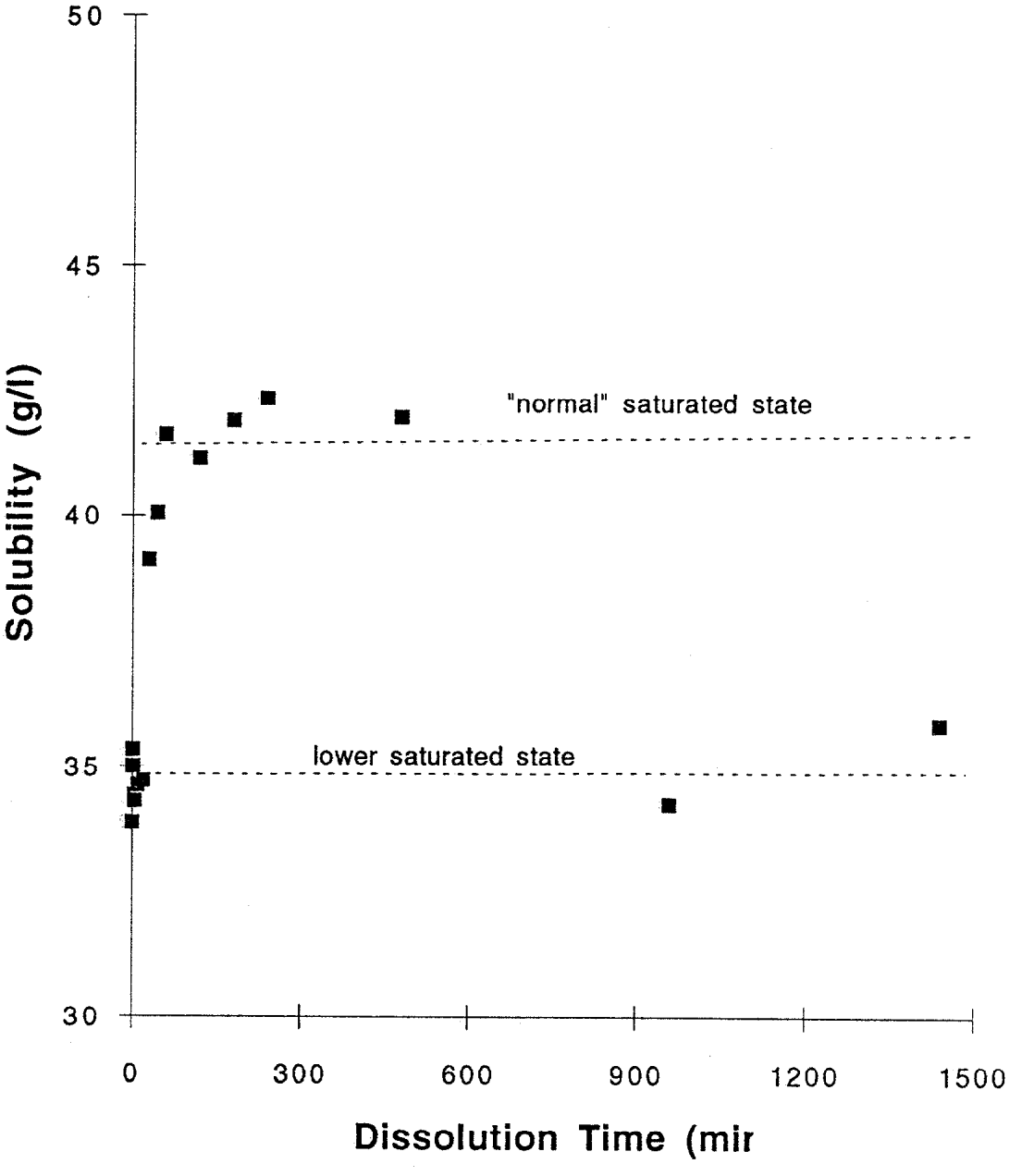

Figure 2-2. Solubility of phosphogypsum sample Gyp-4 *versus* time of dissolution. This curve shows that gypsum dissolves very quickly in EDTA. The solution reaches the theoretical saturated state within the first hour and returns to a lower apparent solubility after about 8 hours.

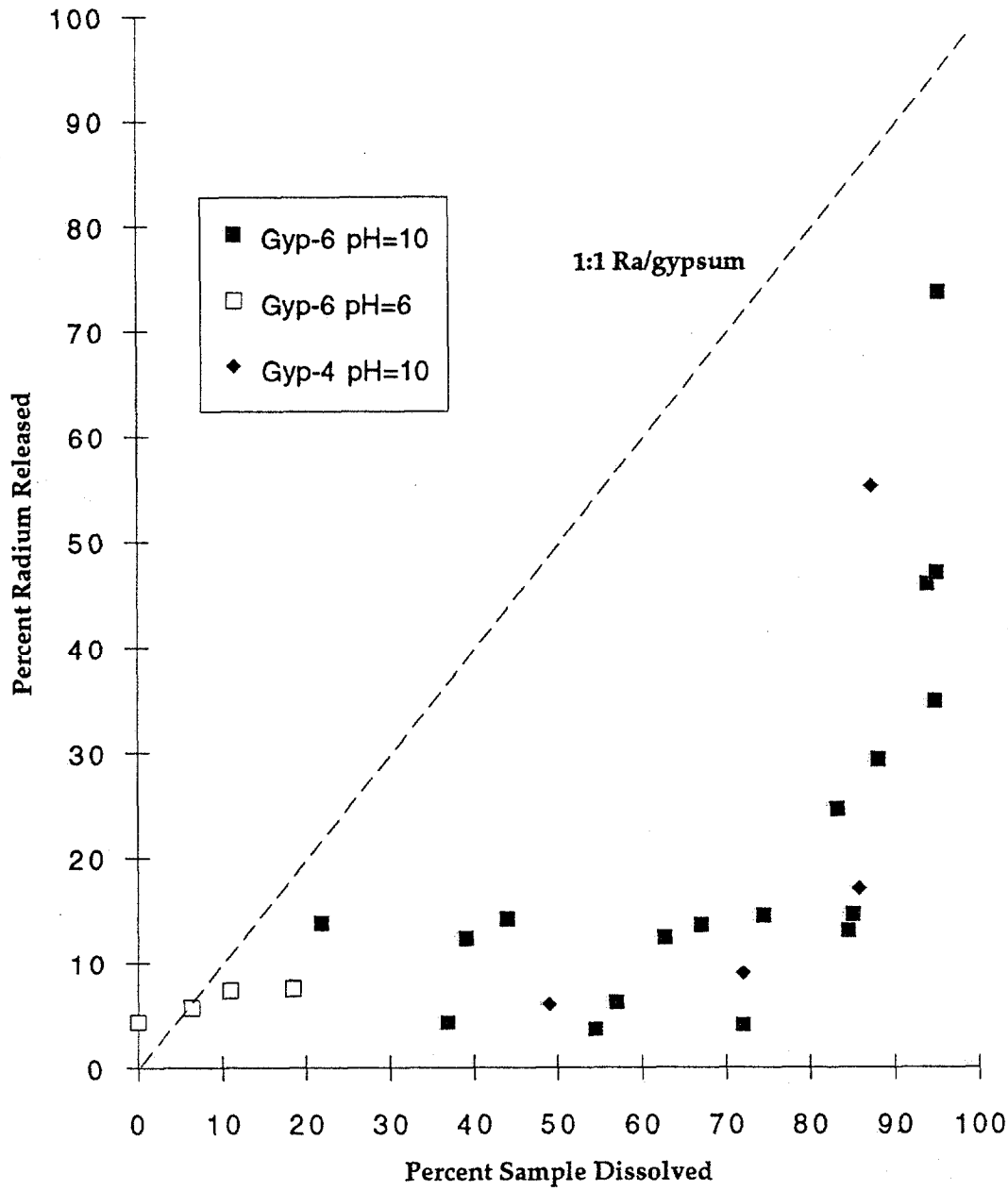

Figure 2-3. Percent ^{226}Ra released into EDTA *versus* percent sample dissolved from phosphogypsum samples Gyp-6 at pH=10 (solid symbols) and Gyp-6 at pH=6 (open squares). The 1:1 reference line shows where the data would plot if ^{226}Ra was uniformly distributed as a lattice constituent of $CaSO_4 \cdot n\ H_2O$ and was released during dissolution without any subsequent adsorption.

congruently. If radium is an integral part of the $CaSO_4 \cdot nH_2O$ matrix and no subsequent adsorption or reprecipitation of radium occurs during sample dissolution in EDTA, the data points in this plot should plot along the 1:1 reference line. Instead, the data plot along a flat trend at about 5% radium removal and then increase rapidly around the 90% dissolution point. These results are quite significant and may be interpreted in two different ways. First, EDTA may selectively dissolve low-radium or radium-free $CaSO_4 \cdot nH_2O$ and only begins to attack the radium-enriched fraction of the phosphogypsum when dissolution of $CaSO_4 \cdot nH_2O$ is complete. In this case the phase(s) containing radium must be less soluble than either the dihydrated (DH) or hemihydrated (HH) forms of $CaSO_4 \cdot nH_2O$. Several other sulfates such as barite ($BaSO_4$), celestite ($SrSO_4$), and anglesite ($PbSO_4$) are less soluble than gypsum in most reagents and radium has the least tendency of all alkaline earth metals to form complex ions (Kirby *et al*., 1964). The alternative explanation is that radium is released during $CaSO_4$ dissolution in 0.25M EDTA and reprecipitates or immediately sorbs back onto remaining surfaces until all $CaSO_4 \cdot nH_2O$ is dissolved.

In contrast to the ^{226}Ra results, plots of the percent ^{210}Pb released versus percent sample dissolved (Figure 2-4) do fall along a 1:1 reference line, indicating that ^{210}Pb is apparently released congruently during the dissolution of $CaSO_4$ by 0.25M EDTA. Thus, EDTA is effective in congruently dissolving the ^{210}Pb rich fraction of the gypsum or Pb mineral phase. The divergent behavior of ^{226}Ra and ^{210}Pb may also be explained in a few different ways: (1) ^{226}Ra and ^{210}Pb may exist in different phases; (2) the two nuclides have different tendencies to form EDTA complexes; or (3) they display different adsorptive behaviors during EDTA leaching.

Other solutions were also used to fractionate radium from phosphogypsum. For example, water and dilute HCl can completely dissolve $CaSO_4 \cdot nH_2O$, although these solvents would require larger volumes because of reduced gypsum solubilities in comparison to EDTA. By comparing the various solubility and radium release results, the leaching reagent which is more efficient and cost effective in preferentially concentrating radium and other radionuclides from phosphogypsum can be determined. If most of the radionuclides can be concentrated in the $CaSO_4 \cdot nH_2O$-free fraction of the phosphogypsum which constitutes less than about 5-10% of the bulk material, it should be substantially easier to identify the phase(s) which hosts these nuclides. Results of leaching experiments using dilute HCl, dilute HCl and H_2O_2, and DDW solutions are summarized in Table 2-4. These results indicate that phosphogypsum is more soluble in dilute HCl than in DDW, while DDW is more efficient than dilute HCl in dissolving the radionuclide-depleted phases, *i.e.,* the HCl leaching experiments showed much higher release of ^{226}Ra and ^{210}Pb than the water leaching experimental results. Neither ^{226}Ra nor ^{210}Pb were released in direct proportion to $CaSO_4 \cdot nH_2O$ dissolution in DDW. Since these radionuclides are significantly enriched in the $CaSO_4 \cdot nH_2O$-free residues (discussed in a following

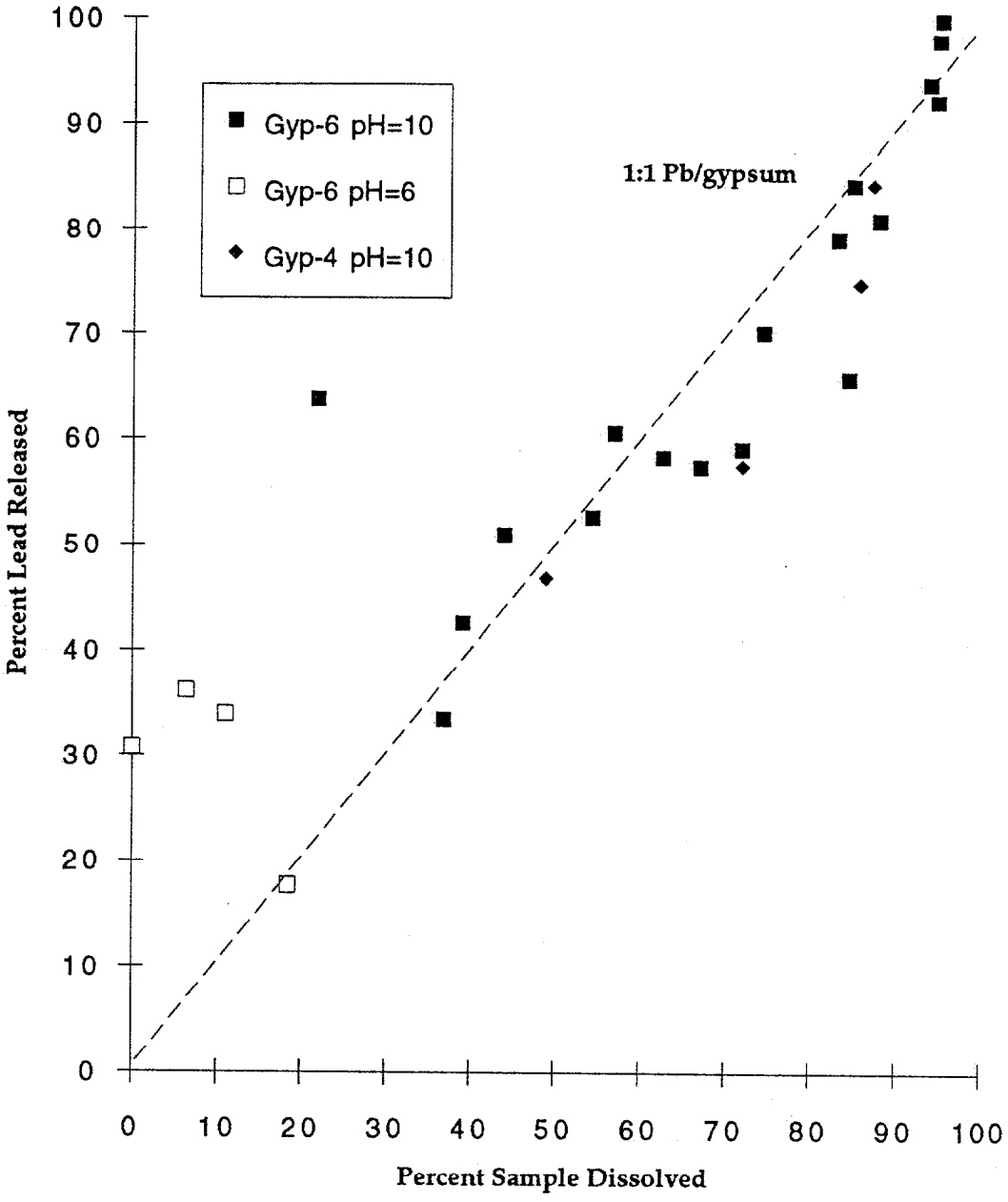

Figure 2-4. Percent ^{210}Pb released into EDTA *versus* percent sample dissolved from two phosphogypsum samples, Gyp-4 and Gyp-6 at pH=10 (solid symbols) and Gyp-6 at pH=6 (open squares). The 1:1 reference line shows where the data would plot if ^{210}Pb was congruently released during the dissolution of $CaSO_4 \cdot n\ H_2O$. This plot is based on radiochemical analysis of ^{210}Pb in the residues remaining after leaching.

Table 2-4. Summary of results of leaching experiments with H_20 and 0.1M HCl. An initial weight of 4.5 grams of sample was used in each case. Errors shown are at the 1σ level based on counting statistics.

Residue Wt (g)	Dissolved (%)	Reagent	Volume (ml)	Dissolution Time (hours)	Residue Activity ^{226}Ra dpm/g	Residue Activity ^{210}Pb dpm/g	Residue ^{226}Ra (%)	Residue ^{210}Pb (%)
				Unfiltered Exp Gyp-6 (DH)				
0.3106	93.10	HCl	2000	5	22± 2	60± 9	3.8± 0.3	11± 2
0.3062	93.20	HCl/H_2O_2	2000/25	5/24	25± 3	30± 7	4.2± 0.4	5± 1
0.5057	88.76	H_2O	2000	5	164± 3	183± 7	45.4± 0.9	54± 2
0.4349	90.34	H_2O/H_2O_2	2000/25	5/24	198± 4	214± 9	46.9± 0.9	54± 3
				Filtered Exp #1 Gyp-6 (DH)				
0.3189	92.91	HCl	2000	5	39± 2	59± 5	6.8± 0.3	11± 1
0.2002	95.55	HCl/H_2O_2	2000/25	5/24	21± 3	50± 10	2.2± 0.3	5± 1
0.4969	88.96	H_2O	2000	5	416± 5	410± 10	100± 2	100± 4
0.3261	92.75	H_2O/H_2O_2	2000/25	5/24	524± 7	543± 16	94± 2	100± 3
				Filtered Exp #2 Gyp-6 (DH)				
0.2265	94.97	HCl	2000	5	24± 2	36± 10	3.0± 0.3	5± 1
0.2146	95.23	HCl/H_2O_2	2000/25	5/24	20± 2	22± 6	2.4± 0.2	3± 1
0.4513	89.97	H_2O	2000	5	363± 7	380± 10	89± 2	98± 3
0.3467	92.29	H_2O/H_2O_2	2000/25	5/24	442± 6	524± 15	84± 4	100± 4

section), both ^{226}Ra and ^{210}Pb may exist, at least partially, in phosphogypsum as a discrete phase(s) rather than substituting in the calcium sulfate lattice. However, re-adsorption of radionuclides by $CaSO_4 \cdot nH_2O$ cannot be ruled out until this is independently evaluated (see next section).

Both ^{226}Ra and ^{210}Pb in samples of Gyp-6 are more soluble in dilute HCl solution than in DDW **(Figures 2-5 to 2-7**). Much of the ^{226}Ra and ^{210}Pb may have been transferred into solution as more soluble $RaCl_2$ and $PbCl_4^{2-}$ complexes. There is a clear fractionation between radium and lead, with lead being more enriched than radium in each residue examined from the H_2O leaching experiments. The fractionation between ^{226}Ra and ^{210}Pb implies that these two radionuclides either exist in phosphogypsum as different phases or display different adsorption characteristics under the experimental conditions. The enrichment factors of ^{226}Ra and ^{210}Pb during leaching increased by 2 to 3 times when the leaching solution was filtered rather than centrifuged to separate insolubles for sample Gyp-6. Compare the unfiltered results (Figure 2-5) to the two replicates which were filtered (Figures 2-6 and 2-7). This indicates that suspended fine particles which have high activities of ^{226}Ra and ^{210}Pb were lost during the unfiltered experiments. Replicate experiments which included filtration for Gyp-6 (Figures 2-6 and 2-7) show good agreement and is thought to be the more accurate representation of the behavior of ^{226}Ra and ^{210}Pb when leached under these conditions. Once again, sorption of radionuclides by $CaSO_4 \cdot nH_2O$ cannot be ruled out in any of the leaching experiments. In order to evaluate which processes control radium solubility in these systems the adsorption characteristics of radium onto phosphogypsum and insoluble residues must be evaluated.

Radium Adsorption Experiments

The results of the previous experiments (Figure 2-3) imply that very little radium is released into solution until the majority of the DH or HH component of phosphogypsum is completely dissolved. However, it is possible that radium is released and "reprecipitates" or immediately sorbs back onto remaining gypsum surfaces (Moore and Scott, 1986). To test this possibility, we conducted a series of tracer experiments. Tracer amounts of ^{226}Ra were added to the leaching experiment and, assuming no reprecipitation or adsorption occurs, should be completely recovered at the end of the experiment. The results of these adsorption experiments **(Table 2-5)** showed that undissolved gypsum adsorbed greater than 95% of tracer radium from EDTA solutions when substantial quantities of DH remained, but dropped to less than 10% adsorption when greater than 88% of the mass of the bulk phosphogypsum sample was dissolved. At that level of dissolution (Exp. #5), virtually no $CaSO_4 \cdot nH_2O$ remained as verified by XRD scans of the insoluble residue. Adsorption experiments at different pH levels showed that the undissolved sample adsorbed more tracer radium from acidic EDTA than in alkaline EDTA solutions.

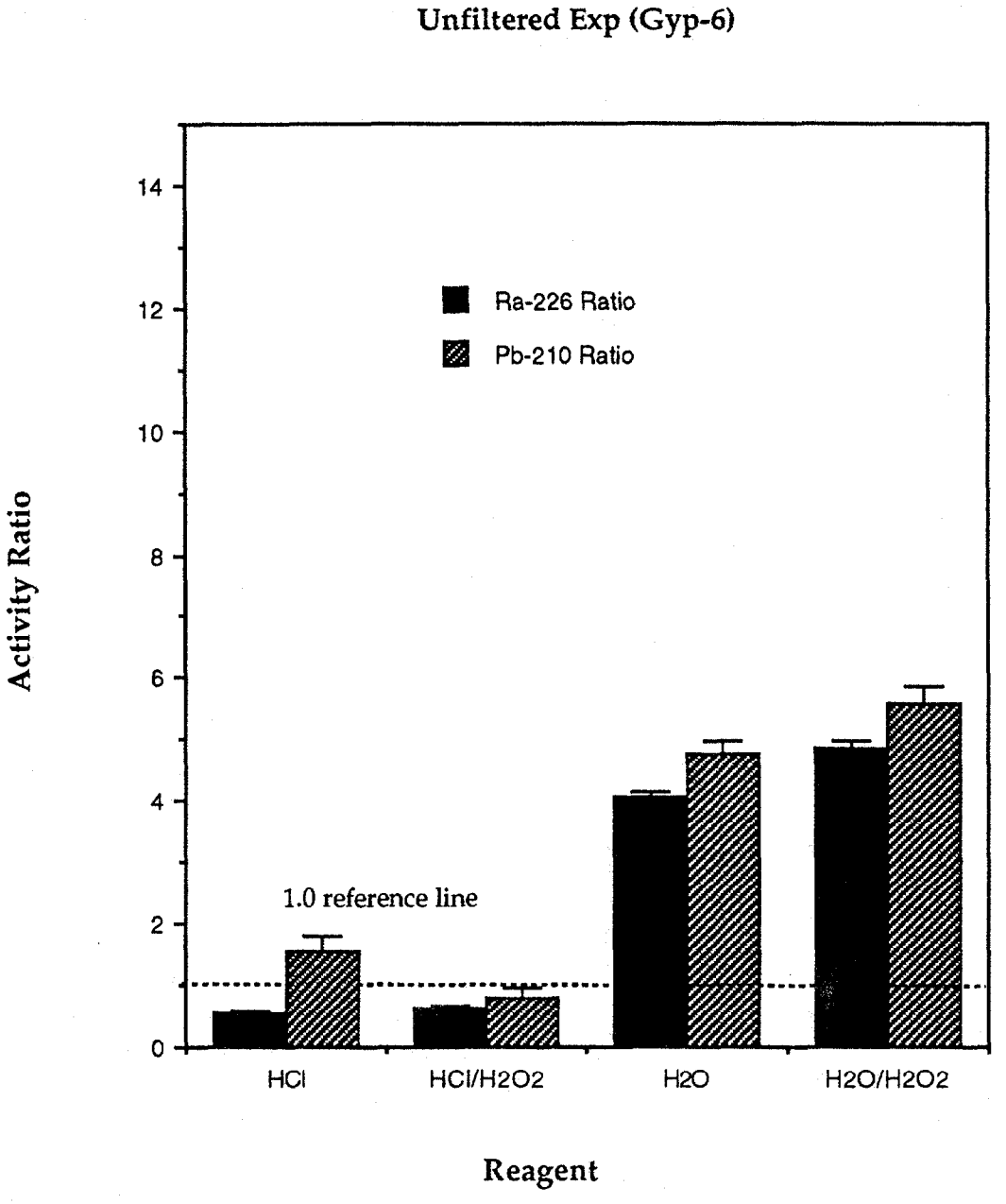

Figure 2-5. Selective leaching results with various reagents for phosphogypsum sample Gyp-6. The enrichment or depletion of ^{226}Ra, expressed as an activity ratio in the residue to that originally present is shown for each of the reagents tested by the black bars. The ^{210}Pb enrichment/depletion is shown by the striped bars. Solutions were unfiltered in these experiments.

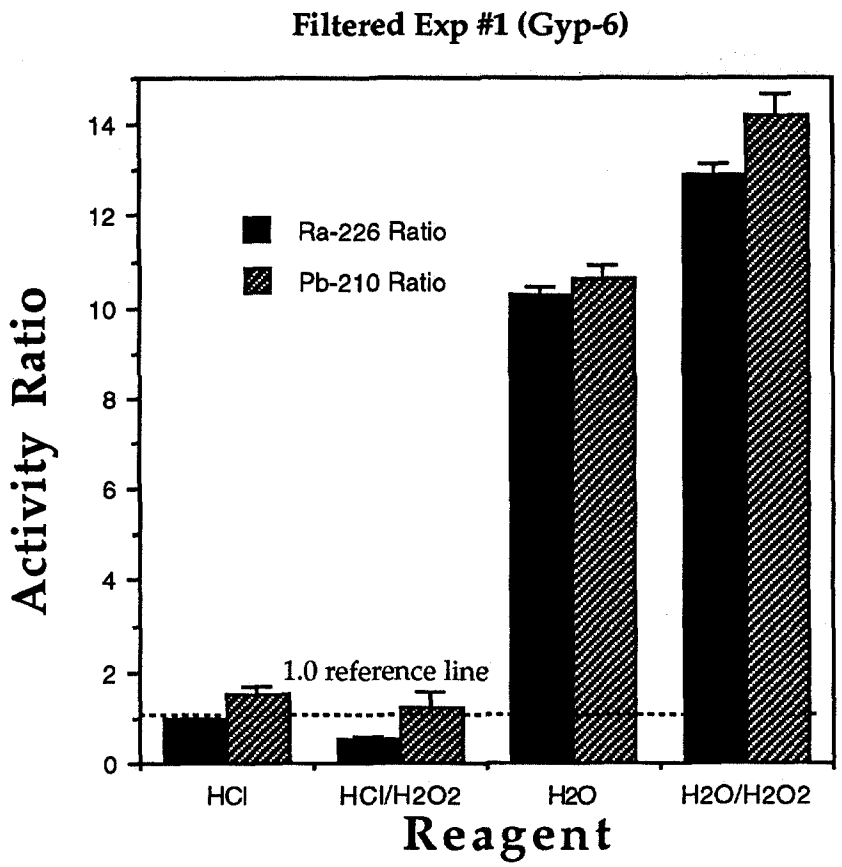

Figure 2-6. Results from a replicate selective leaching experiment with various reagents for phosphogypsum sample Gyp-6. The enrichment or depletion of ^{226}Ra, expressed as an activity ratio in the residue to that originally present is shown for each of the reagents tested by the black bars. The ^{210}Pb enrichment/ depletion is shown by the striped bars. The experimental method was the same here as that shown in Figure 2-5 except that the leaching solutions were filtered in these experiments.

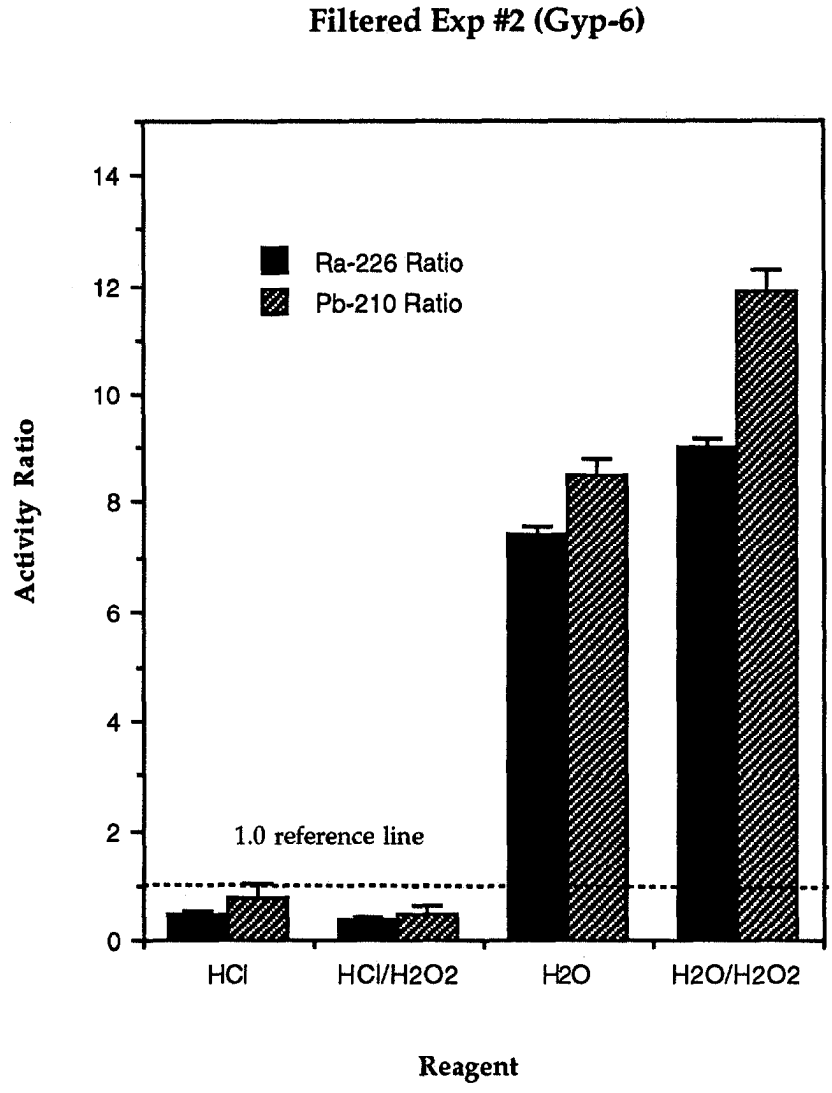

Figure 2-7. Results from a second replicate selective leaching experiment with various reagents for phosphogypsum sample Gyp-6. The enrichment or depletion of ^{226}Ra, expressed as an activity ratio in the residue to that originally present is shown for each of the reagents tested by the black bars. The ^{210}Pb enrichment/depletion is shown by the striped bars. Solutions were again filtered in these experiments.

Table 2-5. Radium adsorption experiment results for different mineral forms of Gyp-6 in 0.25M EDTA and DDW. A known amount (2129 dpm) of ^{226}Ra tracer was added to evaluate adsorption. Each pair of results for the DDW experiments represent duplicate experiments. All errors shown are ±1σ.

Exp. No.	Sample Wt (g)	pH	Volume (ml)	Solution-Ra (dpm)	Dissolved (%)	Adsorbed-Ra (%)
			Gyp-6 (DH) in 0.25 M EDTA			
1	4.4070	10	25	47 ± 3	25.0	97.8 ± 0.1
2	4.4019	10	50	61 ± 5	51.4	97.1 ± 0.2
3	4.4012	10	75	42 ± 4	76.8	98.0 ± 0.2
4	4.4062	10	100	32 ± 3	86.6	98.5 ± 0.1
5	4.4021	10	125	1960 ±80	88.2	8 ± 4
6	4.4042	2	50	6 ± 1	-*	99.7 ± 0.1
7	4.4009	6	50	7 ± 1	-*	99.6 ± 0.1
8	4.4072	10	50	63 ± 5	46.8	97.1 ± 0.2
9	0	10	50	2230 ±100	-**	0 ± 5
			Gyp-6 (DH) in DDW			
10a	4.4018	6	3000	1890±30	92.3	11 ± 2
10b	4.4023	6	3000	2040±20	93.2	4.1 ± 0.7
11a	4.1625	6	2000	1170±30	92.1	45 ± 1
11b	4.1624	6	2000	1220±10	91.6	43.6 ± 0.5
12a	8.3249	6	2000	890±70	64.1	58 ± 3
12b	8.3242	6	2000	960±30	64.5	55 ± 1
			Gyp-6 (HH) in DDW			
13a	4.4041	6	3000	1540±40	89.8	27 ± 2
13b	4.4027	6	3000	1610±10	89.6	24.4 ± 0.6
14a	4.1639	6	2000	970±10	78.3	54.9 ± 0.5
14b	4.1643	6	2000	930±20	78.9	56 ± 1
15a	8.3286	6	2000	800±60	64.9	62 ± 3
15b	8.3293	6	2000	730±20	64.1	66 ± 1

* Sample gained weight, ** no gypsum added.

Radon emanation results of the DDW experiments clearly demonstrate that there is a significant amount of ^{226}Ra adsorption onto the residues while $CaSO_4 \cdot nH_2O$ is still present. The amount of radium adsorption was roughly proportional to the $CaSO_4 \cdot nH_2O$ residue mass, and there appeared to be no significant difference in adsorption by DH versus HH when the sample residues were approximately equal **(Figure 2-8).** As in the case for the EDTA solution experiments, there was clearly a significant decrease in adsorption when $CaSO_4 \cdot nH_2O$ had been completely removed from the phosphogypsum. Note that the fraction dissolved for the experiment with the lowest apparent adsorption (Table 2-5 #10b) was only about 1 percent higher than its counterpart (#l0a) which showed a factor of two greater adsorption. This sharp decrease in radium adsorption implies that solid $CaSO_4 \cdot nH_2O$ is the primary phase which adsorbs radium with very little adsorption occurring on the insoluble residue surfaces.

These experiments verify that the high activity of ^{226}Ra observed in $CaSO_4 \cdot nH_2O$-free insoluble residue fractions (Table 2-5) must be due to a portion of radium being located in separate insoluble phase(s) rather than a result of adsorption of radium released during dissolution of the $CaSO_4 \cdot nH_2O$ phase. These results confirm that a radium-depleted fraction of the phosphogypsum is removed during leaching by both EDTA and DDW. Since both ^{226}Ra and ^{210}Pb are enriched in water-insoluble solid residues after leaching, even when $CaSO_4 \cdot nH_2O$ has been completely removed, a fraction of these nuclides must exist in relatively insoluable mineral phases in the residue despite the fact that adsorption onto $CaSO_4 \cdot nH_2O$ surfaces is important. This confirms that although adsorption of radium is likely to occur during leaching of phosphogypsum if solid $CaSO_4 \cdot nH_2O$ remains, adsorption of radium probably is not significant on the type of insoluble residue present in phosphogypsum. These results indicate that at least a significant portion of the radium exists in phosphogypsum as part of a discrete phase rather than a lattice component in the $CaSO_4 \cdot nH_2O$ crystals or absorbed onto calcium sulfate surfaces.

Leaching experiments of different subsamples of Gyp-6 in two mineral forms yielded some surprising results in terms of the apparent solubilities. Theoretically, HH is approximately twice as soluble at 20°C in DDW than DH. However, the extent of hemihydrate and dihydrate dissolution observed in experiments with DDW are the reverse of what was anticipated based on theory. Subsequent X-ray diffraction analysis of the leaching residues from these experiments showed that only experiment 10b apparently had no solid $CaSO_4 \cdot nH_2O$ remaining. Quartz and apatite were the only two minerals present in the insoluble residue within the XRD detection limit. According to the XRD results, at least some $CaSO_4 \cdot nH_2O$ was still present in all other DDW leaching residues. It is not clear why the apparent solubility of the DH form was greater than the HH. One possibility is that a hydration crust formed around some of the HH grains preventing further dissolution.

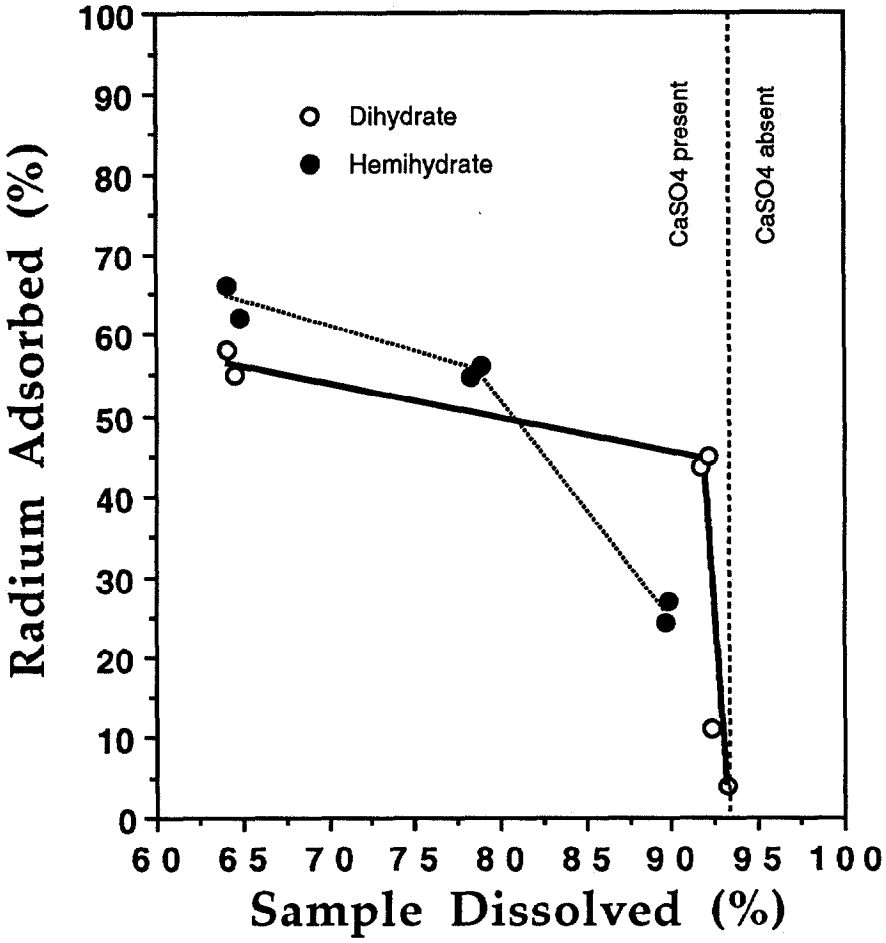

Figure 2-8. Radium adsorption experiment results for the dissolution of two crystalline forms of Gyp-6 in DDW. The proportional decrease in radium adsorption with the amount of undissolved $CaSO_4 \cdot n\ H_2O$ implies that $CaSO_4 \cdot n\ H_2O$ is the primary phase which adsorbs radium. Very little adsorption onto the insoluble residue is indicated.

Activities of Ra-226 in Supernatant Solutions

Activities of Ra-226 in Solutions Analyzed by Radon Emanation

R-Series Experiments

The objective of the initial large-lot dissolution experiments was to produce large quantities of residues. Only the final DDW rinses of water-insoluble residues of bulk samples used to produce insoluble residues in the initial dissolution experiments of Gyp-2, Gyp-4, Gyp-9, Gyp DL3, and Gyp-46 in the "R" dissolution series were retained for analyses of ^{226}Ra in solution. Based upon one of multiple working hypotheses, the activities of ^{226}Ra in these solutions were expected to be low based upon preliminary results of chemical modeling of phosphogypsum dissolved in DDW and previous work on the site(s) occupied by radium in this matrix. Therefore, significant ^{226}Ra in solution was not considered at that time. Approximately 100 L of DDW were used for the dissolution and rinsing of residues of Gyp-9 and Gyp DL3 residues and >180 L used for dissolution and rinse of each of the Gyp-46 samples in the "R" series **(Table 2-6).** The only supernatant solutions that were filtered in "R" series samples were the final rinses of the insoluble residue produced by dissolution of 200 g of Gyp DL3 and samples of Gyp-46 in the "R" series.

It was observed that all the supernatant solutions produced by dissolving bulk phosphogypsum samples in DDW released appreciable portions of ^{226}Ra to solution when virtually all the $CaSO_4 \cdot nH_2O$ phase in bulk samples was dissolved. Activities of ^{226}Ra were low in comparison with the activities of ^{226}Ra in the residues of Gyp-2, Gyp-4, and Gyp DL3. However, only a small fraction of the final rinse solutions in the "R" series were retained and some radionuclides were undoubtedly discarded with the supernatant solutions in these dissolution experiments. There seemed to be a weak trend of higher ^{226}Ra activities in the solutions when a greater mass of bulk sample was dissolved in these initial large lot dissolution experiments. Gyp-46 solutions contained about 65 dpm/L which were the highest activities of ^{226}Ra in supernatant solutions at that time and are about 3 times that of the ^{226}Ra in the leachate of Gyp DL3. There was little or no difference between the activities of ^{226}Ra in the filtered and unfiltered DDW rinse solutions of Gyp-46 residue (Table 2-6).

RAS-Series Experiments

Several additional dissolution experiments were conducted for Gyp-46 and all supernatant solutions were retained. In order to test the reproducibility of analyses of ^{226}Ra in solution, a 50 g sample of Gyp-46 was dissolved in 18.00 L of DDW. The 22-L glass bottle which contained the residues and solution was not disturbed for 10 days following rotation and the supernatant solution contained no visible particulate material or turbidity at the end of this settling period. None of the fine-grained solids at the solid-liquid interface in the 22-L bottle were visibly disturbed during collection of

Table 2-6. Activities of ^{226}Ra in supernatant solutions above water-insoluble residues of Gyp-2, Gyp-4, Gyp-9, Gyp DL3, and Gyp-46 in initial leaching experiments referred to as the "R" series of dissolution experiments. Activities were determined by Rn emanation for portions of the final water rinses which represent only a small portion of the total volume of deionized water used in the dissolutions. Results are the mean of three or more analyses of the same solution (except Gyp-46) and errors quoted represent standard deviations at the 1σ level.

Sample Name	Dissolution Experiment	Sample Dissolved (g)	^{226}Ra in Bulk Sample (dpm/g)	^{226}Ra in Residue (dpm/g)	^{226}Ra in Last Rinse (dpm/L)	Estimate of ^{226}Ra in Total Solution (%)
Gyp-2	Exp 1 - Last Decant	50.0	64.5±0.4	1493±8	7.0±0.2	--
Gyp-4	Exp 2 - Last Decant	50.0	64.6±0.4	--	7.8±0.1	--
Gyp-9	Exp 2 - 3.5 L of ~100 L	200.0	66.3±0.4	1590±20	3.5±0.1	~3
Gyp DL3 R1 Filtered	Exp 4 - 3.5 L of ~100 L	200.0	54.0±0.3	2270±10	24.3±0.1	~23
Gyp-46 R1 Filtered	Exp 5 - 3.0 L of ~180 L	400.0	54.0±0.2	--	64.0±0.6	~53
Gyp-46 R1 Unfiltered	Exp 5 - 3.0 L of ~180 L	400.0	54.0±0.2	--	65.0±0.6	~54

these aliquots. All six aliquots were analyzed for ^{226}Ra in solution and results are given in **Table 2-7.** Activities of ^{226}Ra in the unfiltered samples of Gyp-46 are similar to those in rinse solutions of the initial dissolution experiments of Gyp-46 presented in Table 2-6 even though the dissolution technique was significantly different.

The filtered samples have only slightly lower ^{226}Ra activities than the unfiltered samples (~7%) which implies that >90% of the ~65 dpm/L of ^{226}Ra is in solution if the 0.22μm filter is assumed to effectively remove all particulate material. If this assumption and the additional assumption of solution homogeneity are both valid, 40% of all the ^{226}Ra in the 50.00 g of Gyp-46 used in this dissolution experiment goes into solution. The activity of ^{226}Ra in RAS4F is somewhat higher, but this aliquot was drawn from the second dissolution in which the supernatant solution did not stand for as long prior to the collection of solutions for analysis. Activities of ^{226}Ra were again measured for these solutions subsequent to removing crystalline material which had precipitated in the Rn vessels during repeated de-emanations. These crystallites were removed by filtration and determined by XRD to be gypsum ($CaSO_4 \cdot 2H_2O$). Activities were usually less than 2 dpm/L after the gypsum precipitates were removed and the solutions were again de-emanated and analyzed by Rn emanation (Table 2-7). The low ^{226}Ra activities in solutions which contained very limited masses of gypsum crystallites again demonstrates the strong influence of gypsum to either adsorb or incorporate radium. Incorporation of the radium into the gypsum lattice is not likely based on previous experiments and thermodynamic considerations.

D-Series Experiments

Experimental techniques for subsequent phosphogypsum dissolution experiments were modified to enable detailed mass-activity-composition balances to be constructed (see Experimental Procedures section). These dissolution experiments (the "D-series" in **Table 2-8**) used bulk samples of phosphogypsum which have been well characterized radiochemically and compositionally. Activities of ^{226}Ra in solution were analyzed for 3 filtered and 3 unfiltered aliquots of solutions produced by dissolving 25.0 g of Gyp-6, Gyp DL3, and Gyp-46 in 18.0-L of deionized water. Filtered samples were passed through 0.45 μm polypropylene filters and one sample of Gyp-46 was filtered with a 0.10 μm filter. The mean activities of 3 aliquots from each filtered and unfiltered solution produced for several dissolution lots of each phosphogypsum sample are shown in **Figure 2-9** as is the percentage of the total ^{226}Ra activities in each bulk phosphogypsum sample that went into solution. The "error bars" for each percentage given are lo of the mean values of ^{226}Ra in solution. Filtered samples are slightly lower in activity than the unfiltered samples (<7%) which implies that greater than 90% of the ^{226}Ra is either in solution or is sorbed on colloidal material that have mean diameters less than 0.45 μm.

Table 2-7. Activities of ^{226}Ra in 4 filtered (F) and 3 unfiltered (U) 2.0 L aliquots of the supernatant solution produced by dissolving 50.0 g of Gyp-46 in 18.0 L of DDW referred to as the "RAS" dissolution experiment. Activities of ^{226}Ra in solution were measured by Rn emanation. Errors are given at the 1σ level based on counting statistics only. Solutions were reanalyzed after fine-grained gypsum that precipitated from solutions over a period of three months were removed by filtration.

Sample Name	Type of Filter	Activity of ^{226}Ra in Solution (dpm/L)	Remarks
	Gyp-46 - 50.00 g Dissolved in 18.00 L of Deionized Water		
RAS 1 F	0.22μm Fiber	61.9±0.9	
RAS 1 F ppt.	0.45 μm Poly.	3.9±0.2	2nd Analysis - ppt. removed
RAS 1 U	Unfiltered	62.4±0.9	
RAS 1 U ppt.	0.45 μm Poly.	0.9±0.1	2nd Analysis - ppt. Removed
RAS 2 F	0.22μm Fiber	57.9±0.9	
RAS 2 F ppt.	0.45 μm Poly.	1.6±0.2	2nd Analysis - ppt. Removed
RAS 2 U	Unfiltered	62.2±0.9	
RAS 2 U ppt.	0.45 μm Poly.	0.39±0.09	2nd Analysis - ppt. Removed
RAS 3 F	0.22μm Fiber	62.6±0.9	
RAS 3 F ppt.	0.45 μm Poly.	0.09±0.05	2nd Analysis - ppt. Removed
RAS 3 U	Unfiltered	60.8±0.9	
RAS 3 U ppt.	0.45 μm Poly.	0.17±0.06	2nd Analysis - ppt. Removed
RAS 4 F	0.22μm Fiber	71±1	No re-analysis

Table 2-8. Activities of ^{226}Ra in supernatant solutions and percentages of ^{226}Ra in the bulk samples that went into solution for "D" series dissolution experiments. All samples were prepared by dissolving 25 g of phosphogypsum in 18 L of DDW. All filtered (F) and unfiltered (U) aliquots were analyzed by Rn emanation, but not all unfiltered solutions were analyzed for each dissolution experiment. All ^{226}Ra activities are the means of analyses of three 2 L aliquots removed from the 18 L solution. Errors are standard deviations of the activities in the three aquiluots given at the 1σ level.

Sample Name	Type of Filter	Activity of ^{226}Ra in Solution (dpm/L)	% of ^{226}Ra in Solution
		Gyp-46	
Gyp-46 D2F	0.10μm Poly.	47±2	63±3
Gyp-46 D2 F	0.45μm Poly.	48±2	64±3
Gyp-46 D2 U	Unfiltered	52±2	69±3
Gyp-46 D3 F	0.45μm Poly.	51.5±0.8	69±1
Gyp-46 D3 U	Unfiltered	53±3	71±4
Gyp-46 D4 F	0.45μm Poly.	60±3	80±4
Gyp-46 D4 U	Unfiltered	58±2	78±3
Gyp-46 D7 F	0.45μm Poly.	71±8	90±10
		Gyp-DL3	
Gyp DL3 D1 F	0.45μm Poly.	30±5	40±7
Gyp DL3 D1 U	Unfiltered	30±4	40±5
Gyp DL3 D2 F	0.45μm Poly.	29±5	39±7
Gyp DL3 D2 U	Unfiltered	33±5	44±7
Gyp DL3 D3 F	0.45μm Poly.	25±4	33±5
Gyp DL3 D3 U	Unfiltered	40±10	50±10
Gyp DL3 D4 F	0.45μm Poly.	32±5	43±7
Gyp DL3 D5 F	0.45μm Poly.	40±10	50±10
		Gyp-6	
Gyp-46 D2F	0.45μm Poly.	27±5	48±9
Gyp-46 D2U	Unfiltered	30±10	50±20
Gyp-46 D3F	0.45μm Poly.	31±3	55±5
Gyp-46 D3U	Unfiltered	33±6	60±10

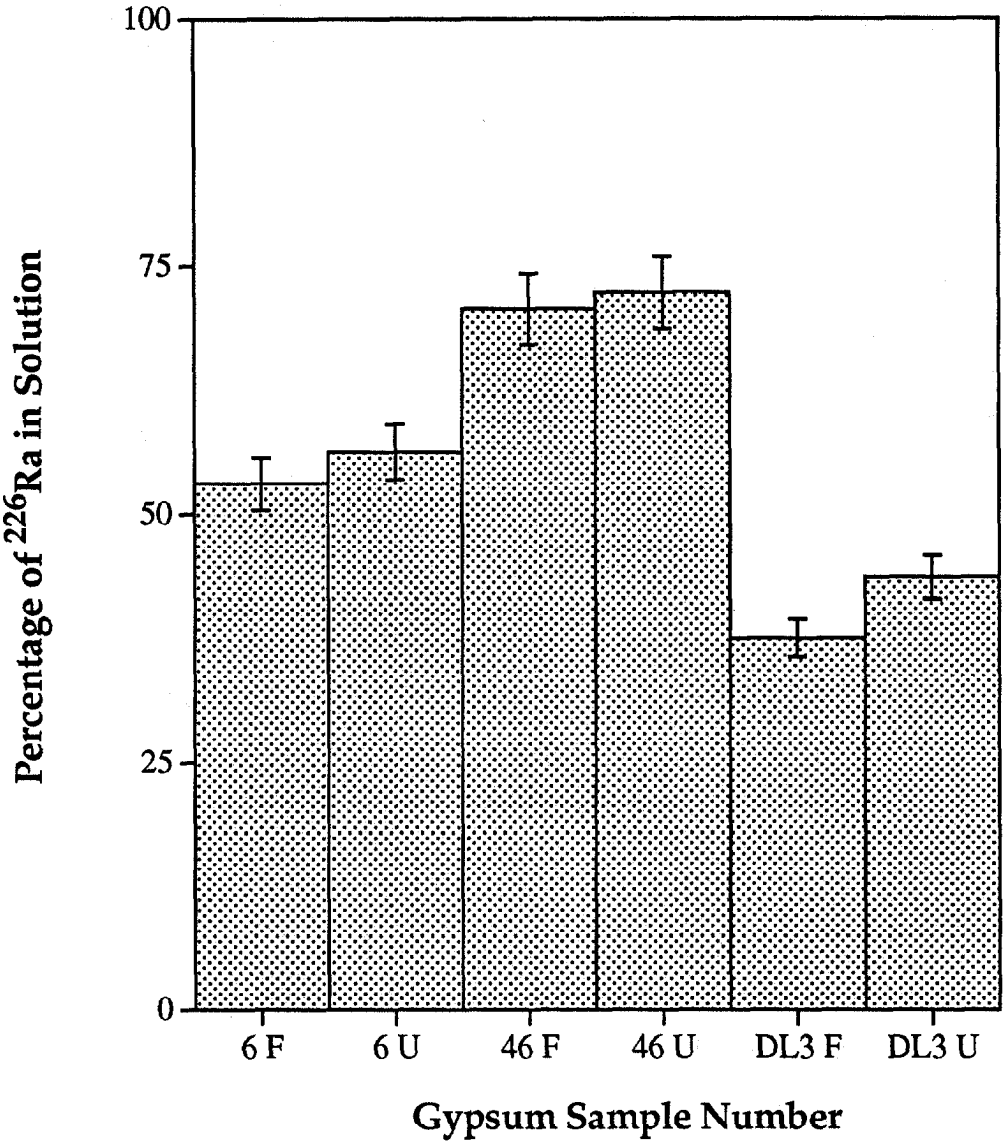

Figure 2-9. Plots of the percentages of ^{226}Ra in solution in "D" series dissolution experiments. Data for both filtered (F) and unfiltered (U) solutions are shown. The percentages plotted are mean values of ^{226}Ra in solution in 2 dissolutions of Gyp-6, 4 dissolutions of Gyp-46, and 5 dissolutions of Gyp DL3. Error bars represent 1σ of the mean values. Activities of ^{226}Ra in solution were measured by Rn emanation.

SD-Series Experiments

Several supernatant solutions of bulk phosphogypsum samples produced in the SD series of dissolution experiments were also analyzed for ^{226}Ra in solution in the same manner. These sample were collected from a number of gypsum stacks in Florida and had been on the stacks for varying periods. The activity of ^{226}Ra in solution for these samples are graphically presented in **Figure 2-10.** Results from these SD solutions clearly indicate that some Florida phosphogypsum samples release significantly more ^{226}Ra into solution when identical leaching procedures are used. Samples in Figure 2-10 are presented in generalized "age" brackets or times since the phosphogypsum samples were placed on the stack. Analyses depicted in Figure 2-10 are averages of three or more Rn emanation analyses of each solution and error bars in this case reflect one standard deviation from the mean value of these analyses. There appears to be a 3-7% decrease in activity when the supernatant solutions are filtered to 0.45 µm and ^{226}Ra, in solution decreased slightly, but not appreciably, in solutions filtered to 0.10 µm.

Although a significant portion of ^{226}Ra in these samples is apparently in solution as defined by the ability to pass through a 0.45 µm filter, radionuclide sorption onto colloids cannot be ruled out. The obvious points are that an large proportion of ^{226}Ra can enter solution for some samples and the release of ^{226}Ra does not seem to be an obvious function of age or sample locality. This suggests that a process other than incorporation of ^{226}Ra in highly insoluble phases controls the activities of ^{226}Ra in solution when all the $CaSO_4 \cdot nH_2O$ is dissolved. As shown earlier, re-adsorption of ^{226}Ra onto $CaSO_4 \cdot nH_2O$ surfaces is important when even minor quantities $CaSO_4 \cdot nH_2O$ were not dissolved or re-precipitated. Re-precipitation of gypsum $(CaSO_4 \cdot 2H_2O)$ did occur in the "R" series when the solutions were de-emanated a number of times in Rn bottles. This was the main reason for dilution and acidification of supernatant solutions in Rn bottles for the "SD" series of dissolution experiments.

PERALS Analyses of Ra-226 Activities in Solutions

Activities of ^{226}Ra were determined by PERALS spectrometry in selected aliquots of supernatant solutions used for Rn emanation analyses. Two aliquots of the same supernatant solution used for dissolutions of Gyp-46 were processed for PERALS analyses. The solution was allowed to stand undisturbed for two days before peristaltically pumping one 3.00-L and another 2.00-L aliquot through an in-line 0.22µm filter with the solution drawn 3-5 cm above the residue-solution interface. A third sample of a supernatant solution above a Gyp-46 residue for PERALS analysis was also filtered with a 0.22µm Millipore fiber filter, but was collected from the upper 10 cm of the solution in a 20-L vessel. Apparent activities of ^{226}Ra in solution were less than 45% of those in same solutions of Gyp-46 which were processed identicallyprior to analysis by Rn emanation (**Table 2-9**). Radium was scavenged from these solutions with $BaSO_4$ precipitates as required for the PERALS analytical technique and extremely fine-grained, light reddish-brown solids were observed within the $BaSO_4$ precipitates.

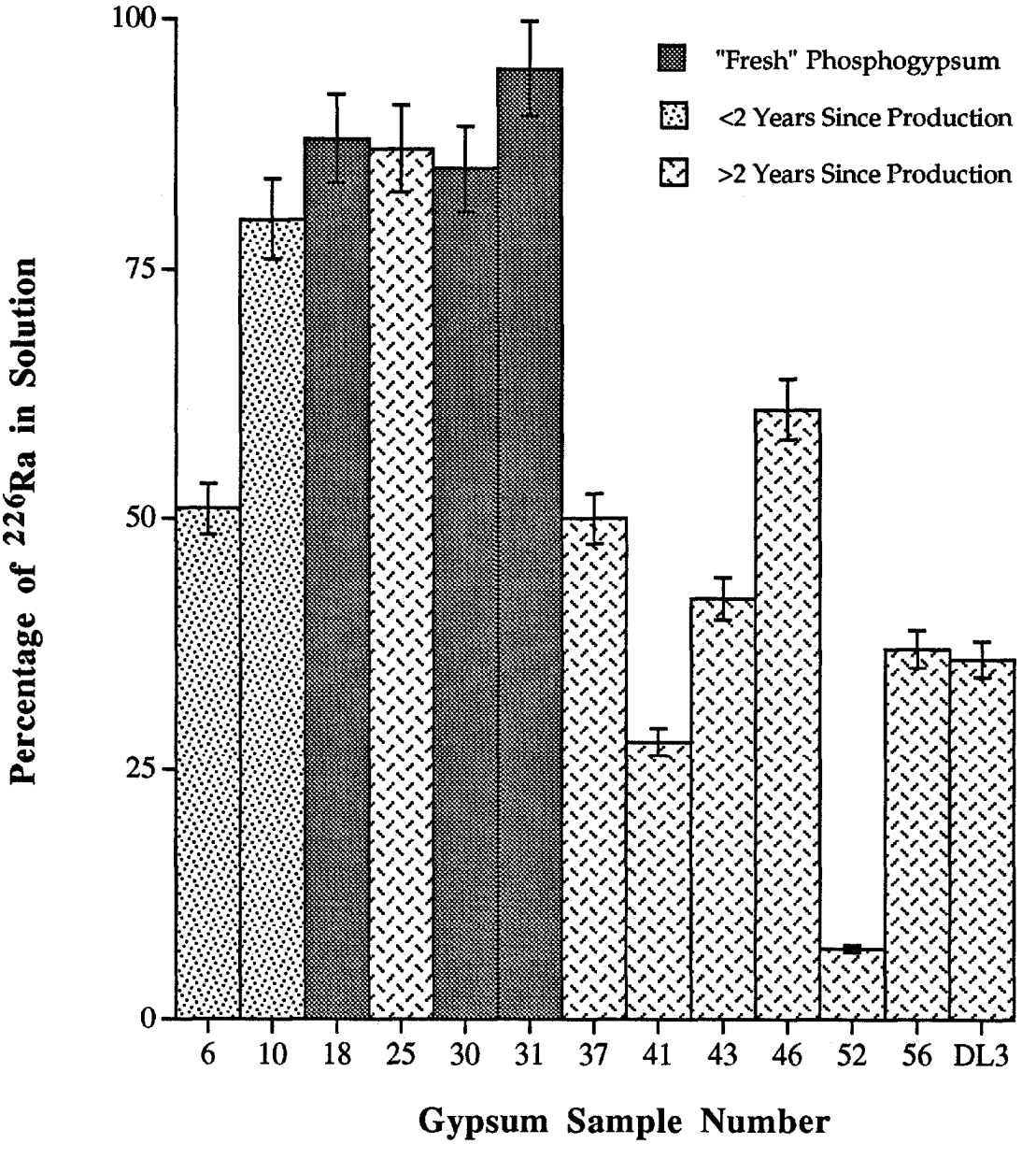

Figure 2-10. Plots of the percentages of ^{226}Ra in solution for "SD" series samples. Solutions were filtered to 0.45 μm and ^{226}Ra in solution was measured by Rn emanation. Percentages are a mean of 3 analyses for each solution and the error bars represent standard deviations at the 1σ level.

Table 2-9. Activities of ^{226}Ra in supernatant solutions above water-insoluble residues of Gyp-46 and Gyp-6. In these experiments activities of ^{226}Ra have been measured by Rn emanation and by PERALS spectrometry. Solutions were either unfiltered, filtered with 0.22μm fiber filters, or filtered with 0.45μm polypropylene filters. Errors are given at the 1σ level based on counting statistics only.

Sample Name	Type of Filter	Analytical Technique	Volume Analyzed	Activity of ^{226}Ra in Solution (dpm/L)
	Gyp-46 - 50.00 g Dissolved in 18.00 L of Deionized Water			
RAS 1 F	0.22μm Fiber	Rn Emanation	2.00 L	61.9±0.9
RAS 2 F	0.22μm Fiber	Rn Emanation	2.00 L	57.9±0.9
RAS 3 F	0.22μm Fiber	Rn Emanation	2.00 L	62.6±0.9
RAS 1 U	Unfiltered	Rn Emanation	2.00 L	62.4±0.9
RAS 2 U	Unfiltered	Rn Emanation	2.00 L	62.2±0.9
RAS 2 U	Unfiltered	Rn Emanation	2.00 L	64.0±0.9
RAS 1 F P	0.22μm Fiber	PERALS	3.00 L	26.0±0.2
RAS 2 F P	0.22μm Fiber	PERALS	2.00 L	26.1±0.1
RAS 3 F P*	0.22μm Fiber	PERALS	3.00 L	18.5±0.2
RAS 4 F*	0.22μm Fiber	Rn Emanation	2.00 L	70.3±0.9
	Gyp-46 - 4.00 g Dissolved in 2.00 L of Deionized Waterr			
Gyp-46FX	0.45 μm Poly.	Rn Emanation	1.87 L	0.92±0.09
	Gyp-6 - 10.00 g dissolved in 14.00 L of Deionized Water			
RAS6 7 F P	0.45μm Poly.	PERALS	2.00 L	0.65±0.01
RAS6 8 F P	0.45μm Poly.	PERALS	2.00 L	3.46±0.02
RAS6 9 U P	Unfiltered	PERALS	2.00 L	0.59±0.01
RAS6 10 F P	0.45μm Poly.	PERALS	1.52 L	0.71±0.03

* Second Dissolution

These fine-grained particles appeared identical in appearance to the finest-grained material observed in water-insoluble residues of phosphogypsum. Upon back extraction of the Ra into the extractant scintillation solution used in this technique, the solution turned dark yellow which is indicative of organic material in the extractant/scintillator solution (J. McDowell, pers. comm.).

Additional PERALS analyses were performed for supernatant solutions above insoluble residues of Gyp-6. Experimental procedures for the dissolution of Gyp-6 are identical to those described above except only 0.45 µm polypropylene filters were used in an in-line filter holder. None of the fine-grained material was observed in $BaSO_4$ precipitates except for an extremely minor amount in the RAS68FP sample which had approximately 6 times the ^{226}Ra activity than the remaining three samples (Table 2-9). Activities of ^{226}Ra in the other three samples of Gyp-6 supernatants analyzed by PERALS contain only ~0.3% of the total ^{226}Ra activity added to the vessel in Gyp-6, assuming the solutions are homogenous. It is surprising that the unfiltered sample (RASP9U) contains the lowest activity, but none of what is believed to be organic material was observed in the $BaSO_4$ precipitate from that solution. Solution RAS610FP was collected as the last liquid was drained from the 20 L vessel. The insoluble residue was disturbed and dispersed throughout the solution when this sample was being filtered, but ^{226}Ra activity in this solution was still <0.3% of that in the total Gyp-6 added to the vessel.

Two lines of evidence point towards the presence of an amorphous or organic phase in the fine-grained material within the $BaSO_4$ precipitates produced for PERALS analyses: (1) color changes due to the presence of what may be carbon being partially absorbed by the toluene-based extractant portion of the scintillator; and (2) lower ^{226}Ra activities calculated by PERALS spectrometry which may be partially due to the presence of organic phases and incomplete extraction of Ra (only ionic Ra^{2+} will extract) and/or color quenching in the scintillator solution. The presence of organic material in the finest-grained residues is also indicated by the amorphous nature of the majority of finest-grained water-insoluble residue analyzed by XRD. If these particles are in fact the same material present in the water-insoluble residues, which is likely, then the 0.22µm filters are ineffective in filtering these particles.

Dissolved Organic Carbon in Supernatant Solutions

Dissolved organic carbon (DOC) was analyzed in three aliquots of supernatant solutions above eight samples of DH and HH phosphogypsum . Aliquots of solutions used for DOC were drawn from the same supernatant solutions analyzed for ^{226}Ra by radon emanation. DOC analyses are given in conjunction with average values of ^{226}Ra in solution in **Table 2-10.** There does not appear to be any obvious relationship between the concentration of DOC and the activities of ^{226}Ra solution of the sort expected if ^{226}Ra were sorbed on organic particles that pass through a 0.45 µm filter.

Table 2-10. Dissolved organic carbon (DOC) concentrations given in parts per million (ppm) and ^{226}Ra activities in supernatant solutions above water insoluble residues of 8 bulk phosphogypsum samples. Supernatant solutions were produced by dissolving about 2.8 g of phosphogypsum in 2 L of DDW. Concentrations are means of 3 analyses of 10 mL aliquots. The activities of ^{226}Ra in solution for each sample are means of 3 or more analyses of a 1 L aliquot of the same supernatant solution used for DOC analyses.

Sample Name	DOC (ppm)	^{226}Ra in Solution (dpm/L)
Gyp 7	9.93±0.09	10.3±0.3
Gyp 10	7.10±0.08	23.8±0.4
Gyp 21	3.85±0.05	102±2
Gyp 30	6.0±0.1	77±3
Gyp 31	5.8±0.3	94±4
Gyp 37	5.5±0.5	56±3
Gyp 54	5.2±0.2	31.6±0.9
Gyp 56	6.0±0.4	23.8±0.4

Insoluble Solid Residues of Bulk Phosphogypsum Samples

Water Insoluble Residues of Gyp-2, Gyp-9, and Gyp DL3

The initial reason for producing relatively large quantities of water-insoluble residues of phosphogypsum was to have enough material to analyze splits for chemical compositions, radionuclide activities, to isolate and identify the material(s) which contain the radionuclides by SEM - XRF, XRD, have adequate amounts of residues for C - N analyses for organic material, and to have enough sample remaining for archiving purposes. The first experiments for measuring the activities of radionuclides in water insoluble residues of phosphogypsum were designed with the objectives of isolating and identifying the mineral phase(s) which contains ^{226}Ra. Residues of Gyp-2 were produced first because at that time the bulk sample had the highest ^{226}Ra activity of the samples analyzed. Activities of ^{226}Ra and ^{210}Pb in bulk samples of Gyp-2 are -64.5 dpm/g and -56.6 dpm/g, respectively, whereas activities of these nuclides in the finest-grained, water-insoluble residue are over 1700 and 2300 dpm/g. Activities of ^{238}U, ^{226}Ra and ^{210}Pb in the water insoluble residues of Gyp-2, Gyp-6, Gyp-9, and Gyp DL3 are given in **Table 2-11.** Activities of ^{226}Ra and ^{210}Pb in the total (fine-grained) and finest-grained fractions of water-insoluble residues display a marked increase in activities relative to bulk samples of unleached phosphogypsum. The activities of ^{226}Ra and ^{210}Pb are highest in the very finest-grained fraction of Gyp-2 as compared to the total insoluble residue which contains mostly quartz, rock fragments, and unreacted ore.

Water Insoluble Residues of Gyp-46 Produced in the “R” and “D” Series

The masses and the percentages of the water-insoluble residues of the five samples of Gyp-46 produced in the "R" and "D" series are given in Table 2-12 and 2-13. Approximately 8 to 9%, with an average value of 8.5%, of Gyp-46 consists of water-insoluble residue in "R" series dissolutions. Variations in the percentages of these residues in the “R” series are believed to result from the time residues were allowed to settle out of the supernatant solutions, minor loses during siphoning and decanting the supernatants. The solute/solvent ratio in the “R” series solutions were selected based on the theoretical solubility of gypsum, but it is possible that the solutions were supersaturated with gypsum during the course of the experiments as additional 50 g lots of the bulk sample were added. Supersaturation of the “R” solutions with apatite and precipitation of poorly crystallized apatite and perhaps some gypsum may have occurred due to the dissolution technique that was used. The 3 rinses of these residues with DDW should have dissolved any residual gypsum. Residues produced in the “D” series contain about 1.5% less insoluble residues than "R" series dissolutions which is not what one would expect if a portion of the “R” series insoluble residues were siphoned off and discarded. Splits of all the residues were x-rayed and gypsum x-ray peaks were not significantly higher in XRD patterns of the “R” residue, but semiquantitative XRD analyses were not performed. Peak shifts and change of intensities for specific XRD peaks are common for hydrated crystals such as gypsum.

Table 2-11. Activities of ^{238}U, ^{226}Ra, and ^{210}Pb measured by gamma spectrometry in the $CaSO_4 \cdot nH_2O$-free residues of Gyp-2, Gyp-9, and Gyp DL3. Residues were produced from leaching experiments with doubly deionized water.

Sample	Sample Description	^{238}U (dpm/g)	^{226}Ra (dpm/g)	^{210}Pb (dpm/g)
Gyp-2 FG	Finest-grained, water-insoluble residue	170±30	1760±20	2380±50
Gyp-2	Fine-grained water-insoluble residue	71±6	1493±8	1400±10
Gyp-6 HH	Finest-grained, water-insoluble residue of Gyp-6 Hemihydrate	68±11	1622±7	3520±20
Gyp-9	Fine-grained water-insoluble residue	7.6±0.4	1590±20	1220±30
Gyp DL3	Finest-grained, water-insoluble residue	180±10	2270±10	4140±20

Table 2-12. Percentages of water-insoluble residues in six bulk samples of Gyp-46 produced in the "R" series of dissolution experiments.

Sample Name	Mass of Bulk Sample Dissolved (g)	Mass of Dry Water-Insoluble Residue (g)	Percentage of Water-Insoluble Residue (%)
Gyp-46 R1	400.0	32.83	8.21
Gyp-46 R2	400.0	34.20	8.55
Gyp-46 R3	450.0	39.64	8.81
Gyp-46 R4	400.0	35.68	8.92
Gyp-46 R5	400.0	31.91	7.98
Mean and 1 Standard Dev.			8.5±0.4

Table 2-13 Percentages of water-insoluble residues in five bulk samples of Gyp-46 produced in the "D" series of dissolution experiments.

Sample Name	Mass of Bulk Sample Dissolved (g)	Mass of Dry Water-Insoluble Residue (g)	Percentage of Water-Insoluble Residue (%)
Gyp-46 D2	25.00	1.692	6.77
Gyp-46 D3	25.02	1.674	6.69
Gyp-46 D4	25.00	1.747	6.99
Gyp-46 D5	24.63	1.883	7.65
Gyp-46 D6	25.00	1.815	7.26
Mean and 1 Standard Dev.	24.9±0.2	1.76±0.09	7.1±0.4

Broad XRD peaks indicative of cryptocrystalline apatite were observed in XRD patterns from both sets of residues.

Percentages of U-238, Ra-226, and Pb-210 in "R" and "D" Series Insoluble Residues

Specific activities of ^{238}U, ^{226}Ra, ^{210}Pb, and ($^{210}Pb/^{226}Ra$) activity ratios given in **Tables 2-14** and **2-15**. The specific activities of ^{238}U are somewhat lower in the "R" residues which could be due to loss of fine-grained, uranium-bearing apatite when the solutions were siphoned off. The specific activities of ^{226}Ra are variable in both sets of residues, but trend to decrease in later dissolution experiments. This is also the case for specific activities of ^{210}Pb in "R" and "D" sets of residues and is likely related to the time the suspended residues were allowed to settle out of the mixtures. The ($^{210}Pb/^{226}Ra$) activity ratios within each set of residues are similar which tends to confirm the settling times are the predominant controlling factor in the amount of radionuclides that are retained. The most notable difference between the "R" and "D" residues are the mean ($^{210}Pb/^{226}Ra$) activity ratios with the "R" series ratio at 0.83 whereas the ratio for the "D" series is about 1.20.

The differences between the "R" and "D" residues of Gyp-46 are further demonstrated in **Table 2-16** and **Table 2-17** which present the percentages of ^{238}U, ^{226}Ra, ^{210}Pb activities retained in the water-insoluble residues. These percentages were calculated by averaging the specific activities of ^{226}Ra and ^{210}Pb in two vials that contained splits of each residue, multiplying this mean value by the mass of water-insoluble residue, dividing these values by the total activities of ^{226}Ra and ^{210}Pb in the bulk sample of Gyp-46, and converting these factors to a percentage. These calculations show that about 43-71% of 238U, 62-69% of ^{226}Ra, and 54-59% of the ^{210}Pb activities are not present in these water-insoluble residues. The percentages of ^{226}Ra in solution in the "D" series supernatant solutions (Table 2-8) and the percentages of ^{226}Ra retained in the residues of Gyp-46 D2, D3, and D4 (Table 2-17) total to about 100% within error with the exception of D4 which totals to about 115±9%. These results support the hypothesis that significant proportions of the ^{226}Ra were either dissolved, sorbed or included within fine-grained particles (less than 0.45 μm).

The "R" series of residues retained more ^{226}Ra and less ^{210}Pb than the "D" series residues. The D-series residues were produced using a different dissolution technique (see Experimental Procedures section) in which all supernatant solutions were retained and the starting solute/solvent ratio of 1.38 g of phosphogypsum per liter of DDW allowed, at least theoretically, for complete dissolution of the gypsum. Two processes could be responsible for the differences in the percentages of ^{226}Ra and less ^{210}Pb in the "R" series residues. More gypsum with sorbed radium may have remained in the "R' series residues, as discussed above, hence the higher mean specific activity and retention of ^{226}Ra in the "R" residues. The appreciably higher specific activities and percentage of ^{210}Pb in the "D" series ratios may be due to either retention of fine-

Table 2-14 Specific activities of ^{238}U, ^{226}Ra, ^{210}Pb, and ($^{210}Pb/^{226}Ra$) activity ratios in $CaSO_4 \cdot 2H_2O$-free, water-insoluble residues of Gyp-46 "R" series dissolution experiments. The mean value of two counting vials are given for Gyp-46 (R1) - (R5). and standard deviations are given at the 1σ level.

Sample Name	^{238}U (dpm/g)	^{226}Ra (dpm/g)	^{210}Pb (dpm/g)	($^{210}Pb/^{226}Ra$) Activity Ratio
Gyp-46 R1	19±2	326±2	278±4	0.85±0.01
Gyp-46 R2	20±2	316±2	277±4	0.88±0.01
Gyp-46 R3	20±2	270±2	217±4	0.80±0.02
Gyp-46 R4	21±2	269±1	221±3	0.82±0.01
Gyp-46 R5	20±2	296±2	244±4	0.82±0.01
Mean and 1 Standard Dev.	20±1	300±30	250±30	0.83±0.03

Table 2-15 Specific activities of ^{238}U, ^{226}Ra, ^{210}Pb, and ($^{210}Pb/^{226}Ra$) activity ratios in $CaSO_4 \cdot 2H_2O$-free, water-insoluble residues of Gyp-46 "D" series dissolution experiments.

Sample Name	^{238}U (dpm/g)	^{226}Ra (dpm/g)	^{210}Pb (dpm/g)	($^{210}Pb/^{226}Ra$) Activity Ratio
Gyp-46 D2	23±2	302±9	335±9	1.11±0.05
Gyp-46 D3	33±2	280±20	340±20	1.2±0.1
Gyp-46 D4	25±2	270±10	330±10	1.22±0.06
Gyp-46 D5	17.6±0.7	220±10	280±10	1.27±0.07
Gyp-46 D6	27.0±0.8	240±10	280±10	1.17±0.07
Mean and 1 Standard Dev.	25±6	260±30	310±30	1.19±0.07

Table 2-16. Percentages of ^{238}U, ^{226}Ra, ^{210}Pb retained in water- insoluble residues Gyp-46 R(1)-(5) produced in the "R" series of dissolution experiments. Percentages are calculated by dividing the total activity of the radionuclide in the insoluble residue by the total activity in the bulk samples of Gyp-46.

Sample Name	Percentage of ^{238}U Retained	Percentage of ^{226}Ra Retained	Percentage of ^{210}Pb Retained
Gyp-46 R1	34	50	45
Gyp-46 R2	45	42	38
Gyp-46 R3	29	46	37
Gyp-46 R4	31	59	41
Gyp-46 R5	30	42	36
Mean and 1 Standard Dev.	34±6	48±7	39±4

Table 2-17 Percentages of ^{238}U, ^{226}Ra, ^{210}Pb retained in water-insoluble residues Gyp-46 D(2)-(6) produced in the "D" series of dissolution experiments. Percentages are calculated by dividing the total activity of the radionuclide in the insoluble residue by the total activity in the bulk samples of Gyp-46.

Sample Name	Percentage of ^{238}U Retained	Percentage of ^{226}Ra Retained	Percentage of ^{210}Pb Retained
Gyp-46 D2	33	38	45
Gyp-46 D3	57	35	45
Gyp-46 D4	35	35	46
Gyp-46D5	28	31	43
Gyp-46 D6	41	33	41
Mean and 1 Standard Dev.	40±10	34±2	44±2

grained phases or colloids that contain a mineral phase that has lead as a essential component or sorbed on the grain surfaces. These results add to the body of evidence that ^{226}Ra and ^{210}Pb are contained in different minerals phases or have difference sorption characteristics in the phosphogypsum matrix. However, direct comparisons of the "R" and "D" residues can easily be misinterpreted since the "R" dissolution experiments were effectively open chemical systems whereas the "D" series were closed.

Water Insoluble Residues of Gyp DL3 and Gyp-6 Produced in the "D" Series

The percentages of water insoluble residues by mass, specific activities of ^{238}U, ^{226}Ra, and ^{210}Pb and the percentages of these nuclides retained by water insoluble residues of Gyp DL3 and Gyp-6 are given in **Tables 2-18, 2-19,** and **2-20**, respectively. The percentage of the water insoluble residues were almost twice as high in the three bulk samples of Gyp DL3 than in Gyp-6 which is most likely due to the amount of detrital quartz sand in the two bulk samples. The specific activities of ^{226}Ra in both samples were similar, but the specific activity of ^{238}U and ^{210}Pb were appreciably higher in the Gyp-6 sample. These differences are reflected in the $(^{210}Pb/^{226}Ra)$ activity ratios which agree quite well for replicates of the same bulk samples. The activity ratios of $(^{210}Pb/^{226}Ra)$ for these phosphogypsum samples were are much greater than unity as were the replicate samples of Gyp-46 in the "D" series experiments. These ratios and the percentages of the ^{210}Pb that were retained in water insoluble residues of these samples, about 100% of the ^{210}Pb in the bulk sample of Gyp DL3 and about 87% of that in the bulk sample of Gyp-6, indicates that retention of more ^{210}Pb than ^{226}Ra by water insoluble residues of Gyp-46 was not anomalous. In fact, the activity of ^{210}Pb retained by these samples is almost twice the activity of ^{226}Ra so the $(^{210}Pb/^{226}Ra)$ ratios in residues of Gyp-46 may be anomalously low.

Distribution of Radionuclides in the Coarser- and Finer-grained Residues

The percentages of ^{238}U, ^{226}Ra, and ^{210}Pb in water insoluble residues that were fractionated into two general grain-sizes by suspension techniques in the "D" series of dissolution experiments are given in **Table 2-21**. These results agree with data presented in Table 2-11 and strongly support the hypothesis that the great majority of radionuclides in the phosphogypsum are contained by the finest-grained residue. It is possible that there is a re-distribution of radionuclides during the dissolution experiments. However, radium sorption experiments indicate that the radium is not incorporated in the crystalline lattice of $CaSO_4 \cdot nH_2O$.

Table 2-18 Percentages of water-insoluble residues in bulk samples of Gyp DL3 and Gyp-6 produced in the "D" series of dissolution experiments.

Sample Name	Mass of Bulk Sample Dissolved (g)	Mass of Dry Water-Insoluble Residue (g)	Percentage of Water-Insoluble Residue (%)
Gyp DL3 D1	25.00	2.442	9.77
Gyp DL3 D2	25.02	2.490	9.96
Gyp DL3 D3	24.97	2.488	9.96
Gyp-6 D2	24.98	1.395	5.58
Gyp-6 D3	25.00	1.402	5.61

Table 2-19 Specific activities of ^{238}U, ^{226}Ra, ^{210}Pb, and ($^{210}Pb/^{226}Ra$) activity ratios in $CaSO_4 \cdot 2H_2O$-free, water-insoluble residues of Gyp DL3 and Gyp-6 in "D" series dissolution experiments. The mean values and standard deviation are given at the 1 σ level for activities and activity ratios in the D series residues.

Sample Name	^{238}U (dpm/g)	^{226}Ra (dpm/g)	^{210}Pb (dpm/g)	($^{210}Pb/^{226}Ra$) Activity Ratio
Gyp DL3 D1	70±10	300±20	470±20	1.6±0.1
Gyp DL3 D2	78±5	290±10	470±10	1.62±0.09
Gyp DL3 D3	97±6	310±10	480±10	1.50±0.08
Gyp-6 D2	230±20	320±20	590±20	1.8±0.1
Gyp-6 D3	200±20	350±20	590±20	1.7±0.1

Table 2-20. Percentages of ^{238}U, ^{226}Ra, ^{210}Pb retained in water-insoluble residues Gyp DL3 D(1)-(3) and Gyp-6 D2 and D3 produced in the "D" series of dissolution experiments. Percentages are calculated by dividing the total activity of the radionuclide in the insoluble residue by the total activity in the bulk samples.

Sample Name	Percentage of ^{238}U Retained	Percentage of ^{226}Ra Retained	Percentage of ^{210}Pb Retained
Gyp DL3 D1	120±40*	55±3	100±4
Gyp DL3 D2	140±60*	53±3	101±3
Gyp DL3 D3	120±30*	57±3	101±3
Gyp-6 D2	82±4	44±2	87±3
Gyp-6 D3	88±4	48±2	87±3

* Activities of ^{238}U calculated from ^{234}Th were near the lower limits of detection in for ^{234}Th by γ- spectrometry in the IG well detector.

Table 2-21. Distribution of ^{238}U, ^{226}Ra, ^{210}Pb in the two grain-size fractions of water-insoluble residues of Gyp-46 D2-D6, Gyp DL3 D1-D3 and Gyp-6 D2 and D3 produced in the "D" series of dissolution experiments. Nuclides in the coarser-grained residue (referred to as "Solids") and the finest-grained suspended material (SM) fractions are given as percentages of the total radionuclide activities retained by the water insoluble residues

Sample Name	% of ^{238}U		% of ^{226}Ra		% of ^{210}Pb	
	in Solids	in SM	in Solids	in SM	in Solids	in SM
			Gyp-46			
Gyp-46 D2	23±4	80±10	7±1	93±4	15±1	85±4
Gyp-46 D3	20±3	80±10	8±1	92±9	16±1	84±9
Gyp-46 D4	20±5	80±9	7±1	93±6	14±1	86±6
Gyp-46 D5	43±9	60±20	18±1	82±6	25±1	75±6
Gyp-46 D6	39±5	61±9	21±1	79±6	29±1	71±5
			Gyp DL3			
Gyp DL3 D1	7±3	93±9	8±1	92±7	10±1	90±7
Gyp DL3 D2	16±3	84±7	10±1	90±6	13±1	87±6
Gyp DL3 D3	22±7	78±9	23±2	77±5	24±1	77±5
			Gyp-6			
Gyp-6 D2	16±3	84±7	6±1	94±7	4±1	96±7
Gyp-6 D3	22±7	78±9	4±1	96±7	3±1	97±7

Chemical Compositions and Radionuclide Activities in Leached Phosphogypsum

FSU (Gyp DL3) Experiment

To ensure the validity and replicability of experiments relating the chemical compositions with radiochemistries of bulk sample and leachates of phosphogypsum, a large quantity of phosphogypsum sample Gyp DL3 was air-dried, desiccated to constant mass, ground to a fine powder, homogenized, and split into two sub-samples. Phosphogypsum from each bulk sample split was analyzed by XRD to confirm that only the DH phase was present prior to preparation of samples for compositional and gamma spectrometric analyses. Activities of ^{238}U, ^{226}Ra, and ^{210}Pb in replicate samples of bulk Gyp DL3 were measured by γ-spectrometry. Specific activities of these nuclides are given for replicates of the bulk sample (FSU-4 and FSU-5) in **Table 2-22**. The activities of ^{226}Ra and ^{210}Pb agree within the lo precision. The specific activity of ^{238}U is near the lower limit of detection for this sample using this analytical technique. Six samples of the Gyp DL3 phosphogypsum were prepared: FSU-1 is the finest-grained, water insoluble residue and FSU-2 is the coarser-grained insoluble residue produced from the dissolution of 70.0 g of bulk Gyp DL3, split 1. FSU-3 is the water insoluble residue (not fractionated by grain-size) produced by dissolution of a 60.0 g sample of split 2 of the bulk Gyp DL3 bulk sample. FSU-4 and FSU-5 are bulk, air-dried samples taken from Gyp DL3 split 1 and split 2, respectively. FSU-6 is a sample of Gyp DL3 Split 1 that was 75% dissolved (by mass) in DDW. Specific activities of ^{238}U, ^{226}Ra, and ^{210}Pb in the FSU samples are presented in Table 2-22. Once again, the highest specific activities of ^{238}U, ^{226}Ra, and ^{210}Pb are associated with the finest-grained water insoluble residue.

Relationships of Radionuclides to Chemical Compositions

The fractions of Gyp DL3 described in the preceding section and splits of the five replicate samples of Gyp-46 produced in the "R" series of dissolution experiments of Gyp-46 (RES 1-5) were used to relate the chemical compositions of bulk, partially dissolved, and water insoluble residues of phosphogypsum to radionuclide activities. Three additional residues of Gyp DL3 have been analyzed for chemical compositions and radioactivities; the finest-grained residue of a replicate sample of bulk Gyp DL3 (RES-7), and water insoluble residues of two more bulk samples (RES-8 and RES-9). We assumed that if different fractions produced from large phosphogypsum samples were treated separately, they would have varying amounts of the minor chemical components. By tracking the elemental and radiochemical relations within and between these samples which were chemically and mechanically fractionated, we should be able to assess which phases are most important in terms of controlling the radiochemical content. Although the approach is indirect, it is a way of determining important relations within these samples which would not be possible by analysis of single samples. Concentrations of chemical components in these samples **(Appendix C)** have been converted to units of millimoles or micromoles per gram of sample so atomic ratios can be considered.

Table 2-22. Activities of ^{238}U, ^{226}Ra, and ^{210}Pb measured by γ-spectrometry in FSU 1 to 6 samples (Gyp DL3). FSU-1, 2, and 3 are water insoluble residues, FSU-4 and 5 are replicate bulk samples, and FSU-6 is a sample of Gyp DL3 which had about 75% of the mass dissolved.

Sample	Sample Mass (g)	Sample Description	^{238}U (dpm/g)	^{226}Ra (dpm/g)	^{210}Pb (dpm/g)
FSU-1	0.140	Finest-grained, water insoluble residue	183±13	2272±12	4135±24
FSU-2	2.759	Coarse-grained, water insoluble residue	9.7±1.0	75.0±0.7	155.2±1.7
FSU-3	2.516	Total water insoluble residue	26.3±2.2	176.0±1.3	382.9±3.3
FSU-4	1.868	Bulk, air-dried phosphogypsum, Split 1	1.6±0.3	53.6±0.5	45.5±1.0
FSU-5	1.792	Bulk, air-dried phosphogypsum, Split 2	0.5±0.1	54.2±0.3	46.3±0.6
FSU-6	0.906	~75% Dissolved (by wt.). Split 1	3.3±0.6	109.2±1.0	109.3±1.8

Plots of Ba versus ^{226}Ra and Ba versus ^{210}Pb are shown in **Figures 2-11 (A)** and **(B)**. The Ba correlated with both ^{226}Ra and ^{210}Pb quite well. Unfortunately, samples from the residues produced from the two bulk samples had a tendency to cluster into a few groups which can cause artifacts in correlating parameters. Activities of both radionuclides were concentrated in the finest-grained residues of Gyp DL3 and Gyp-46 which also had the highest concentrations of Ba. Activities of ^{210}Pb in the finest-grained residues were about twice those of ^{226}Ra for similar concentrations of Ba. This trend is consistent with the results given in Table 2-11 for the finest-grained water insoluble residues of Gyp-2, 6, 9, and DL3 and ^{210}Pb activities in the finest-grained residues of Gyp DL3 shown in Table 2-22. Plots of Ce and La *versus* ^{226}Ra are shown in **Figure 2-12 (A)** and **(B).** These rare earth elements demonstrated the best correlations with ^{226}Ra activities of any chemical components that were investigated. The activities of ^{210}Pb were observed to be about twice that of ^{226}Ra for similar concentrations of Ce and La.

Divalent cations and rare earth elements were not the only elements which demonstrated close correlations with these radionuclides. **Figures 2-13 (A)** and **(B)** are plots of Al and P versus ^{226}Ra activities. Although the correlations of these elements with ^{226}Ra were not at strong as the rare earths, the finest-grained residues contained the most Al, P, and radionuclides. The P/^{226}Ra ratios appeared to remain fairly constant for the majority of the residues and finest-grained residues. The plots of Al *versus* P and Fe *versus* P shown in **Figures 2-14 (A)** and **(B)** also displays a good relationship between these elements. The samples of each bulk phosphogypsum sample were grouped into two discrete clusters for all but the finest-grained residues in Figure 2-14 (A), but the correlation is stronger for Fe/P ratios plotted in Figure 2-14(B). This implies that phases that contained a fixed ratio of Fe/P were present in the samples. This trend was the strongest for the finest-grained residues.

Figure 2-15 demonstrates a trend could not be produced if the majority of the ^{226}Ra in these samples of phosphogypsum was included in $BaSO_4$. The Ba and ^{226}Ra in these samples correlated quite well with ^{226}Ra (Figure 2-11(A)) as did Al (Figure 2-13(A)). When Ra and Al were more abundant in the sample, so was ^{226}Ra. The finest-grained water insoluble residues contain more Al, Ba, Fe, and P and the highest activities of ^{226}Ra. However, Figure 2-15 demonstrates that the Al remaining in the solids increased much less than Ba when the samples were leached with DDW. As the (Ba/Al) molar ratios decreased, the ^{226}Ra remained relatively unchanged until the majority of the water soluble fraction (predominantly gypsum) was dissolved. Once all the water soluble material was dissolved, the activity of ^{226}Ra increased and the (Ba/Al) molar ratio remained fairly constant. Exactly the opposite trend would be expected if the ^{226}Ra were included in $BaSO_4$ because it is a not an aluminum-bearing mineral phase. Therefore, the insoluble ^{226}Ra in phosphogypsum appears to be associated with an aluminum-bearing mineral phase, perhaps an aluminum phosphate. Figure 2-15 also implies that there must be a non-radiogenic barium phase in the phosphogypsum.

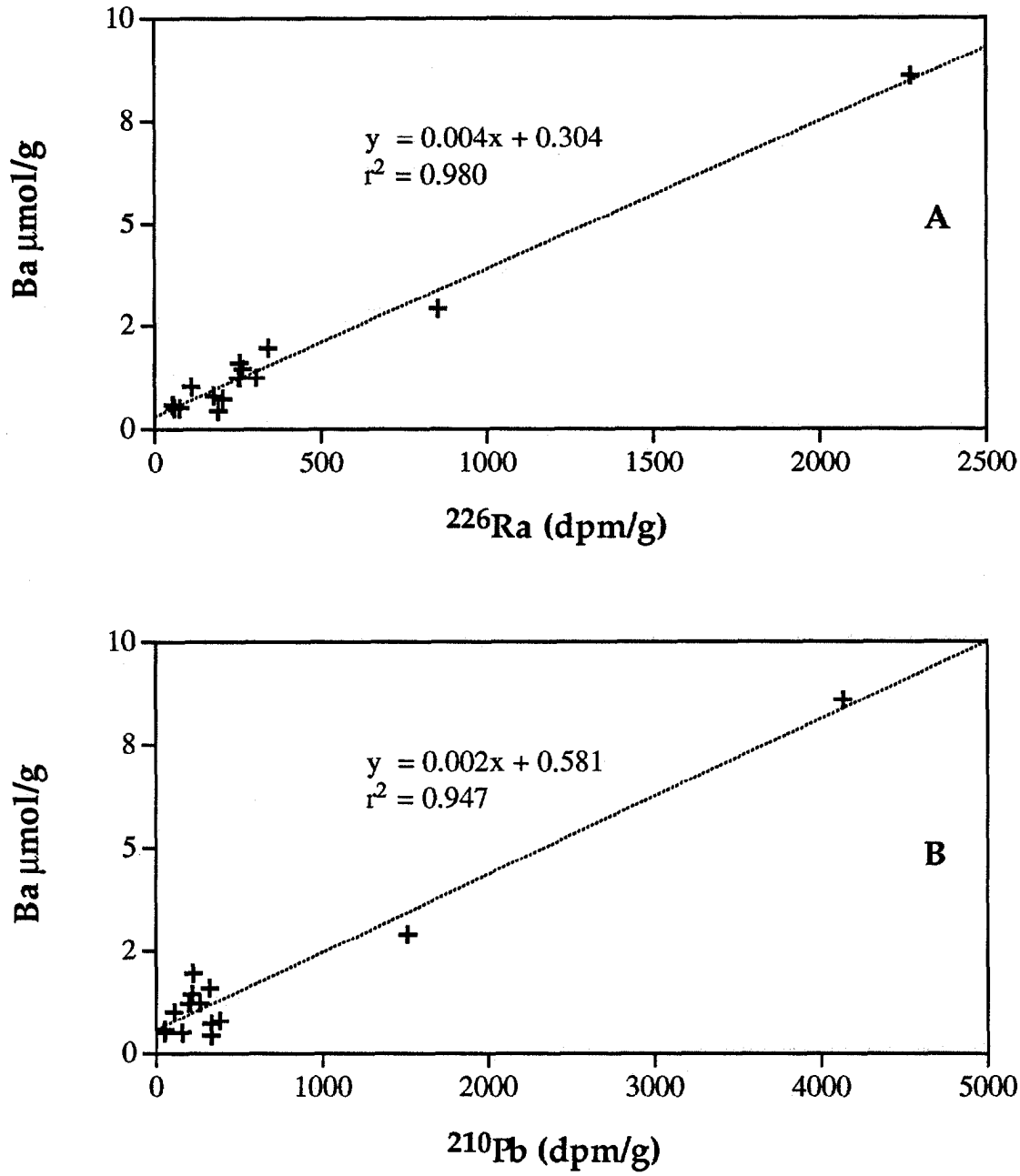

Figure 2-11. **A.** Plot of Ba (µmol/g) *versus* ^{226}Ra (dpm/g).

B. Plot of Ba (µmol/g) *versus* ^{210}Pb (dpm/g).

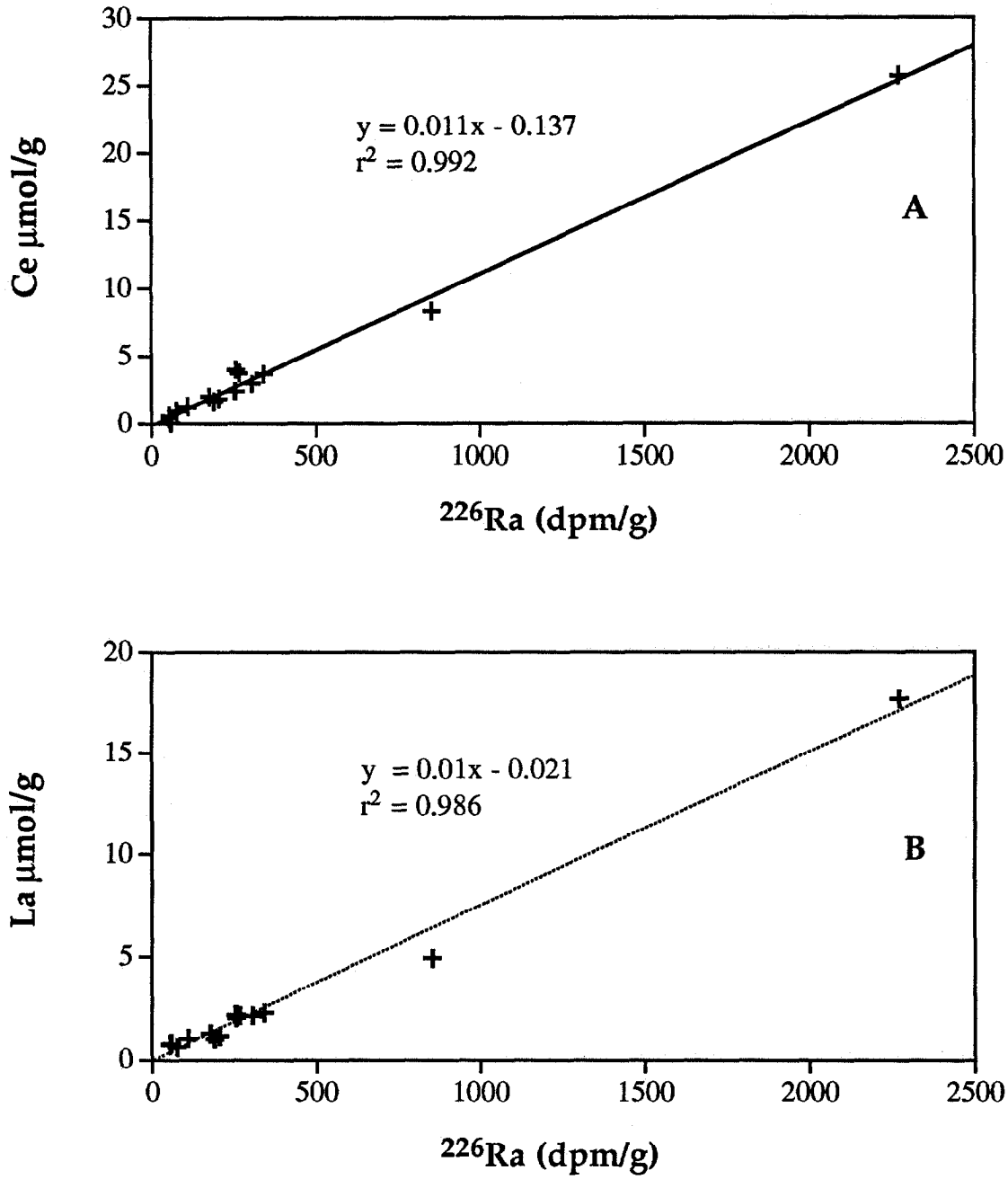

Figure 2-12. **A.** Plot of Ce (µmol/g) *versus* ^{226}Ra (dpm/g).

B. Plot of La (µmol/g) *versus* ^{226}Ra (dpm/g).

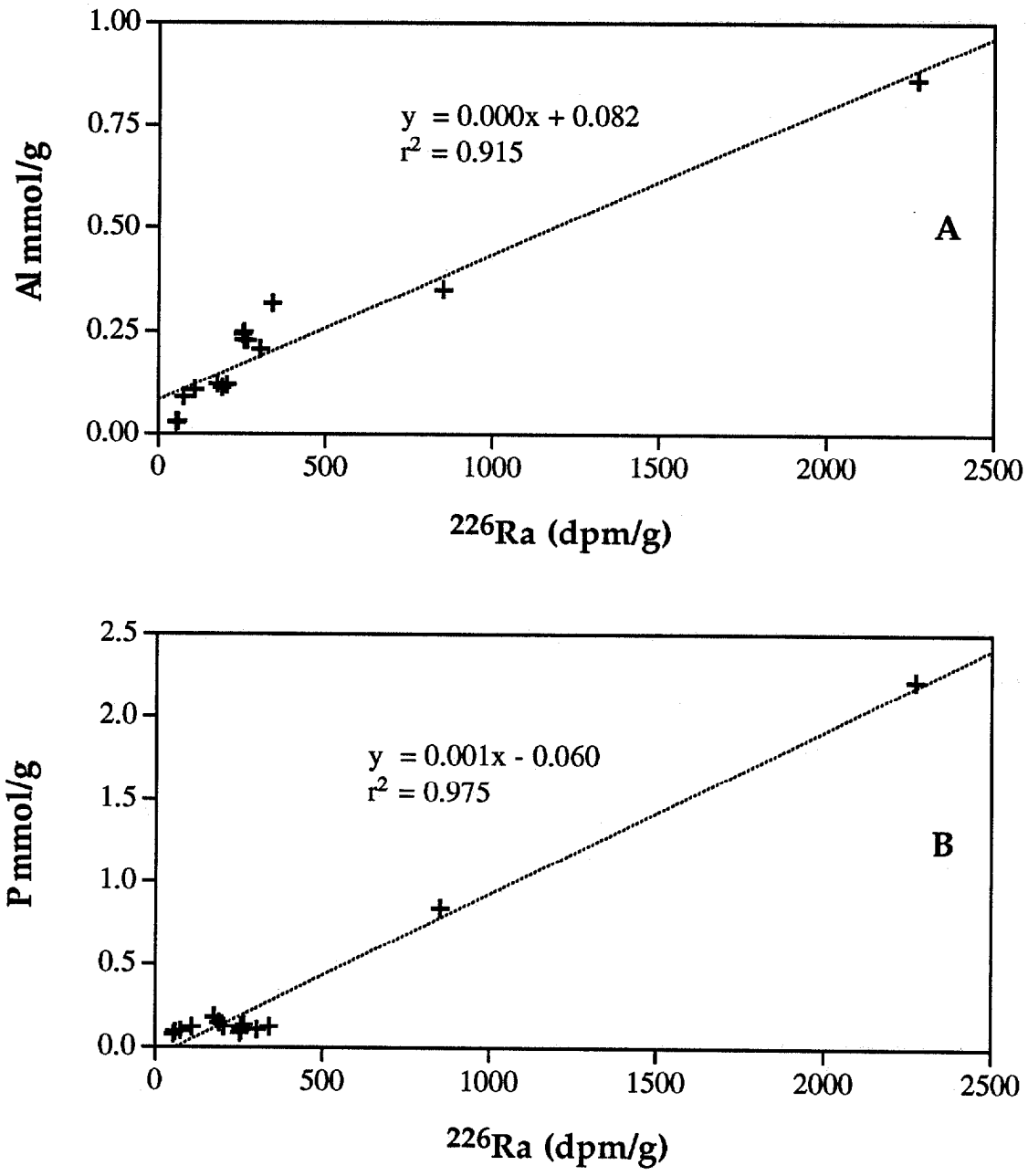

Figure 2-13. **A.** Plot of Al (mmol/g) *versus* ^{226}Ra (dpm/g).

B. Plot of P (mmol/g) *versus* ^{226}Ra (dpm/g).

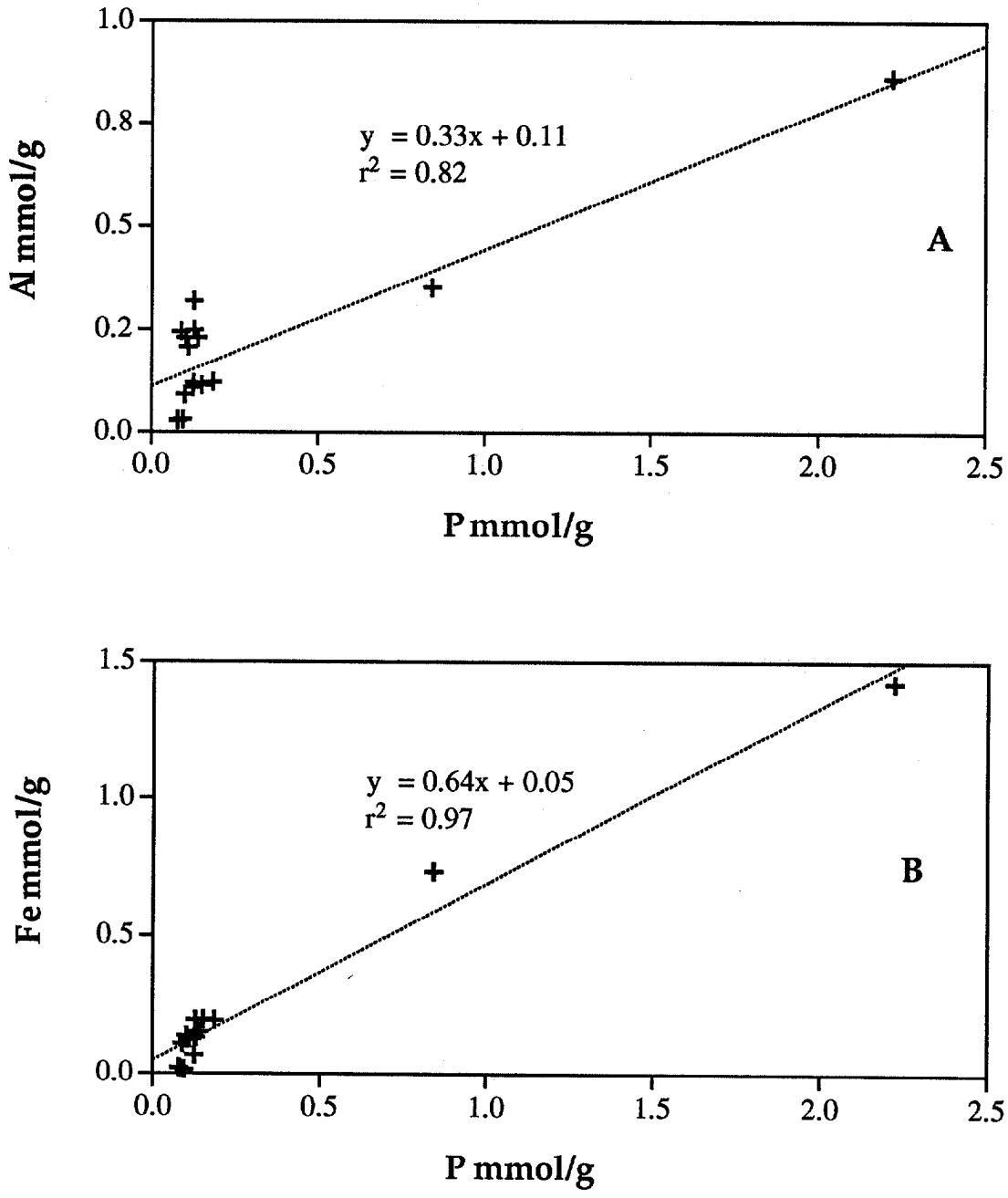

Figure 2-14. **A.** Plot of Al (mmol/g) *versus* P (mmol/g).

B. Plot of Fe (mmol/g) *versus* P (mmol/g).

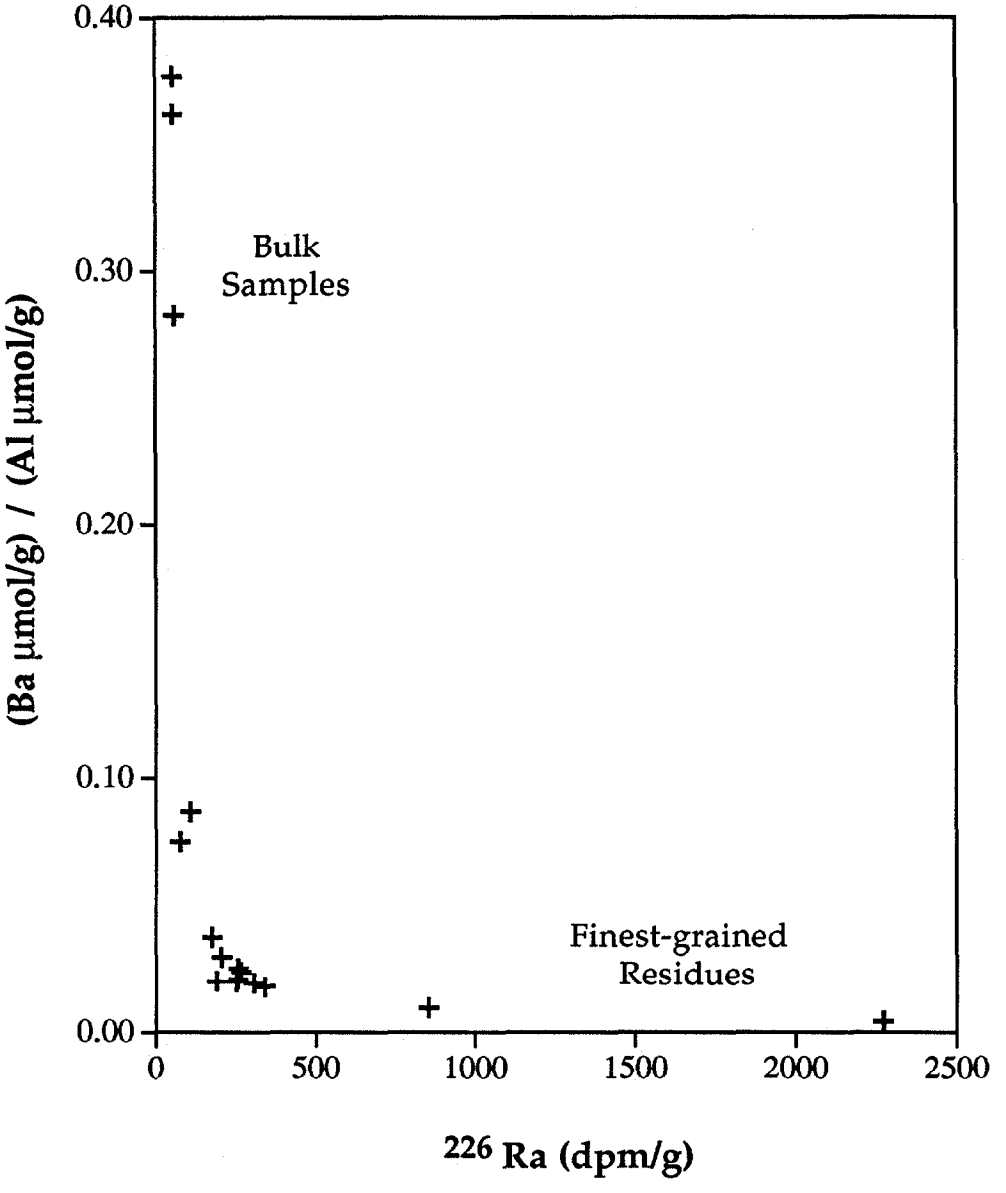

Figure 2-15. Plot of (Ba µmol/g) / (Al mmol/g)*versus* ^{226}Ra (dpm/g).

Although the presence of water insoluble sulfates may still be important in terms of hosting radium and other radionuclides, it appears that most (and potentially all) of the ^{226}Ra and ^{210}Pb in phosphogypsum may be associated with an aluminum-rich phase. Based on the elemental relationships reported here and the chemical compositions of our most radium-enriched residues, it appears that the carrier phase for the insoluble portion of the radium may have a composition similar to the mineral crandallite, $CaAl_3(PO_4)_2(OH)_5 \cdot H_2O$. This mineral, found in nature as a low-temperature weathering product of carbonate fluorapatite, is known to contain appreciable amounts of Sr, Ba, Fe, and rare-earth elements. Presumably, radionuclides such as ^{226}Ra would be able to substitute into the structure of this mineral in the same lattice position as Ba and Sr. Positive identification of this or other phases will require more sophisticated phase separation techniques to isolate the mineral(s) of interest.

One or more F bearing phases must also be present in the phosphogypsum in addition to the residual apatite. A $(Na_X,K_{1-X})_2SiF_6$ phase has been observed growing in zones of cooling water discharge on the gypsum stacks. The F in this phase is quite high stoichiometrically so these discharging solutions must contain high concentrations of F. Another line of evidence that one or more water-insoluble F-bearing phase(s) in contained in the bulk phosphogypsum is suggested by compositional data for FSU-6 (Appendix C). About 75% of the mass of the FSU-6 sample was dissolved in DDW and the residue contains a higher (F / P) ratio than the bulk samples (FSU-4 and 5). It is possible that fluoride phases such as CeF_3, LaF_3, and perhaps CaF_2 in the phosphogypsum matrix also include radionuclides.

X-ray Diffraction Results

Water insoluble residues of phosphogypsum dissolution experiments (samples without DH or HH) have been analyzed by XRD to identify the minerals phases present. XRD patterns have been produced for bulk samples and numerous grain size and mass fractions as well as the finest-grained fractions of water insoluble residues of five phosphogypsum samples (Gyp-2, Gyp-6, Gyp-9, Gyp-46, and Gyp-DL3). These XRD results indicate that the most abundant mineral phases in DDW insoluble residues are quartz (silica sand) and cryptocrystalline apatite, most likely a carbonate fluorapatite $[Ca_5(PO_4, CO_3)_3(F)]$. Quartz comprises the greatest proportion of the total residues and is always detected by XRD. The fluorapatite is extremely fine-grained and the cryptocrystalline nature of this phase, indicated by very broad peaks in the XRD patterns, infers that this apatite has been reprecipitated from the acidic solutions in the reaction vessels rather than representing the primary mineral within the ore rock. Aluminum phosphates and complex calcium and iron aluminophosphate patterns were infrequently identifiable in finest-grained residues when all the gypsum was dissolved and most the quartz had been removed. No other mineral phases, except for quartz, could be positively identified in the total or the finest-grained fractions of the water-insoluble residues using the XRD unit at Florida State University which has lower limits of detection for mineral phases of about 2 to 3%.

Several of the finest-grained, suspended solids from samples Gyp-6, Gyp DL3, and Gyp-46 collected by centrifugation and on filters have also been analyzed by XRD. XRD patterns provide evidence of multiple phases in the dark "uncentrifugable" fraction of brown, fine-grain sized particles collected on filters. These samples have XRD peaks that are clearly of a different phase(s) than in the finest-grained residue collected by centrifugation. The most intriguing of the XRD patterns are two of the finest-grained solids on 0.10 μm filters used to filter Gyp-46 D3 that were analyzed on the XRD unit at FIPR using the TVA supplemental database for phase identification. These peaks were probably masked in the centrifuged fractions since the phases are highly diluted in the solid fraction. A summary of XRD results obtained using the FIPR instrumentation and software is included as **Table 2-23.** A complex Fe-phosphate and chukhrovite ($Ca_4AlSi(SO_4)F_{13}{\cdot}12H_2O$) have been positively identified in the finest-grained water insoluble residues.

SEM Imagery and Semiquantitative XRF of Residue Fractions

The <0.65 μm fraction of a water insoluble residue of Gyp-2 was the first sample analyzed by Scanning Electron Microscopy (SEM). Extremely fine-grained quartz (SiO_2 - fine silt-sized grains), minor Ca, S, and O ($CaSO_4{\cdot}nH_2O$), and appreciable quantities of Ca, F, P, O, and F were observed although no Ba or Sr were detected. Quartz grains are separated from the finest-grained water insoluble residues by physical means (centrifugation), so the presence of some very fine-grained sand is not surprising. A very minor amount of $CaSO_4{\cdot}nH_2O$, <0.2% of the total mass, was also present.

The compositional analyses of residues produced by XRF are semiquantitative and interpretation is difficult since the area that was excited by the electron beam was relatively large compared to the sizes of the grains of interest. SEM images and semiquantitative compositional analyses have been performed for selected density fractions of residues of Gyp-46 R1, R2, and R3. Crystal habits observed by SEM imagery included the "small balls" mentioned by Moisset, 1990 (more properly referred to as nodular or boytryoidal morphologies) but no SEM imagery was diagnostic of known radionuclide-bearing, inorganic phases. However, there are some intriguing clues yielded by the compositional analyses. One composition which reoccurs is that of a Al, Si, Ca, and Fe bearing material in the >3.30 g/cm^3 fraction of Gyp-46 R3 (**Table 2-24**). A similar composition is noted in the <2.58 g/cm^3 fraction along with minor S. The latter composition could be due to the presence of chukhrovite ($Ca_4SO_4SiAlF_{13}{\cdot}nH_20$) which we have observed in water-insoluble residues of phosphogypsum.

Heavy Liquid Separations of Gyp-46 Residues

Summaries of two heavy liquid separation experiments using Gyp-46 R4, a water insoluble residue produced in the "R" dissolution series, are presented in **Tables 2-25** and **2-26**. Experiment A was performed using the highest specific gravity heavy liquid

Table 2-23. Summary of XRD results of the very finest-grained, water-insoluble residues (the "uncentrifugable fraction") of selected samples of phosphogypsum. Solids were collected on 0.1 μm filters and grains are oriented by size and shape. Extremely fine-grained α-quartz was also identified and amorphous material is likely present in all samples.

Sample Name	Composition of Mineral Phase	Name of Mineral Phase
Gyp-6 D3 SM UCF	$NH_4Fe_3P_6O_{20}\cdot 10H_20$	Complex Fe-Phosphate (TVA XRD Datafile 0-36)
	$Fe_3NH_4H_8(PO_4)_6\cdot 6H_20$	Complex Fe-Phosphate (TVA XRD Datafile 0-14)
	$KSrFe_2(PO_4)_3$ (Tenative ID)	Not Named (TVA XRD Datafile 25-911)
Gyp DL3 D3 SM UCF	$NH_4Fe_3P_6O_{20}\cdot 10H_20$	Complex Fe-Phosphate (TVA XRD Datafile 0-36)
	$NH_4Fe_3P_6O_{20}\cdot 10H_20$	Not Named (ASTM Powder File 31-53)
	$Fe_3NH_4H_8(PO_4)_6\cdot 6H_20$	Complex Fe-Phosphate (TVA XRD Datafile 0-14)
	$KFe_3P_6O_{20}\cdot 10H_20$	Complex Fe-Phosphate (ASTM Powder File 31-1037)
	$Na_3PSO_3\cdot 12H_20$ (Tentative ID)	Not Named (ASTM Powder File 18-1260)
	$(Ce,La)_3Si_{20}O_8OH$ (Very Tentative ID)	Toernebohmite (ASTM Powder File 14-257)
Gyp-46 D3 SM UCF	$Ca_4AlSi(SO_4)F_{13}\cdot 12H_2O$	Chukhrovite (ASTM Powder File 0-20)
	$FePO_4$ (Tentative ID)	Polymorph Not Known (ASTM Powder File 29-715)

Table 2-24. Semiquantitative XRF analyses of material in density fractions of Gyp-46R3 separated with heavy liquids. Compositions are not solely those of the finest-grained materal in most cases. Compositions are given in atomic percent normalized to 100%.

Sample Name	Spectrum Number	Density Range (g/cm^3)	Composition (Atom % of Element)
R3.f3 Mininum Quartz	S14	<2.58	Ca 56.5, Si 25.2, Al 8.6, S 4.1, P 3.4, Fe 1.4
R3.f3	S21	<2.58	Si 36.6, Ca 35.7, P 13.6, Fe 7.3, Al, 4.2, S 2.1
R3.f3 Nodular Debris	S12	2.59-2.75	Ca 82.7, Si 10.1, Al 3.0, S 2.4, Fe 1.7
R3.F1 Zircon	S15	>3.30	Zr 51.0, Si 49.0
R3.f1 Zircon	S16	>3.30	Zr 49.2, Si 49.2, Ca 1.6
R3.f1	S17	>3.30	Si 39.4, Al 28.1, Ca 24.1, Fe 8.3
R3.f1	S18	>3.30	Al 54.0, Si 30.0, Fe 8.3, Ca 5.4
R3.f1	S19	>3.30	Al 56.7, Si 31.2, Fe 9.7, Ca 1.8
R3.f1	S20	>3.30	Fe 37.2, Ti 32.7, P 29.1

Table 2-25. Summary of heavy liquid separation of Gyp-46R4 - Experiment A. The starting material was 1.1058 g of residue with ^{226}Ra activity (relative) of 224±3 dpm/g used in density (ρ) fractionation experiment. Errors are given at the 1σ level based on counting statistics only. See text for explanation.

Density Range (g/cm^3)	Mass in ρ Fraction (g)	% of Mass in ρ Fraction	^{226}Ra in dpm/g of Total Residue	^{226}Ra in dpm/g of ρ Fraction
<2.53	0.331	29.9	126.1±7.7	381±23
2.53-2.67	0.701	63.4	73.5±5.3	105±8
2.67-2.71	0.037	3.3	12.1±2.6	327±70
>2.71	0.014	1.3	6.8±1.3	486±93
Σ	1.083	97.9	218.7±9.8	
	Normalized to 100% Recovery:		223.4±10.0	

Table 2-26. Summary of heavy liquid separation of Gyp-46R4 - Experiment B. The starting material was 1.2090 g of residue with ^{226}Ra activity (relative) of 224±3 dpm/g for the density (ρ) fractionation experiment. Errors are given at the 1σ level based on counting statistics only. See text for explanation.

Density Range (g/cm^3)	Mass in ρ Fraction (g)	% of Mass in ρ Fraction	^{226}Ra in dpm/g in Total Residue	^{226}Ra in dpm/g in ρ Fraction
Water & Acetone Soluble	0.016	1.3	18.2±1.4	1138±88
1.94-2.50	0.090	7.4	20.2±4.1	224±46
2.50-2.55	0.018	1.5	19.8±3.1	1100±172
2.55-2.60	0.033	2.7	19.6±2.2	594±67
2.60-2.65	0.918	75.9	98.6±6.5	107±7
2.65-2.71	0.039	3.2	18.4±3.7	471±95
2.71-2.89	0.045	3.7	20.6±3.6	458±80
>2.89	0.021	1.7	12.7±1.4	604±67
Σ	1.180	97.4	228.1±10.2	
	Normalized to 100% Recovery:		234.2±10.5	

first and then less dense liquids whereas the residue in Experiment B was initially separated with the least dense liquid and then by progressively denser liquids. The activities of ^{226}Ra in Gyp-46 R4 do not agree precisely with those given in Table 14 because calibration of the well type IG γ-ray detector had not been completed when these experiments were conducted. These experimental results remain valid since the relative activities of ^{226}Ra in the density fractions yield the information required to evaluate the data.

Unfortunately, the results of Experiment A are not replicated in Experiment B. The less than 2.53 g/cm^3 fraction in Experiment A contains about 30% of the mass of the total residue and approximately 56% of the total ^{226}Ra activity (Table 2-25). The less than 2.53 g/cm^3 fraction contains some quartz, but most quartz is in the 2.53-2.67 g/cm^3 fraction as expected (α-quartz ρ=2.65 g/cm^3). This fraction contains 33% of the ^{226}Ra, and 63% of the residue mass. There appears to be a systematic relationship of lower ^{226}Ra activities (with respect to the total residue) with increasing density fractions. Results of Experiment B are presented in Table 2-26 and the largest fraction of the ^{226}Ra activity is in the fraction containing quartz and 76% of the mass of the residue. No trend of decreasing ^{226}Ra activity with increasing density is apparent and the distribution of ^{226}Ra activities in density fractions is not similar to results of Experiment A. Experimental procedures were different in that the density fraction separations were performed in reverse order in the two experiments, but SEM examination of density fractions suggests that the major reason for irreproducibility is grain aggregation. This is the same reason that dry and wet sieving could not effectively concentrate radionuclide-bearing phases in grain-size fractions by sieving homogenized bulk phosphogypsum samples.

Total Organic Carbon in Insoluble Residues

One reference in the scientific literature (Ferguson, 1985) mentions that radionuclides are retained by fine-grained, organic material in phosphogypsum. However, none of the statements in this report that refer to radionuclides being sorbed on organic material or the activities of sorbed nuclides were documented. Mineral phases which contain the appropriate stoichiometric proportion of C were included in searches of XRD peaks being used to identify the minor phases in the water-insoluble residues, but none were indicated. Organic phases are usually amorphous and if so, will not produce XRD patterns. The presence of an organic component in the finest-grained solid residues is of importance not only for determining whether sorption is an important process in radionuclide fixation and mobilization, but also because sulfate reducing bacteria (SRB) cultured from samples of Florida phosphogypsum require carbon in their metabolic cycle. The roles of bacteria in fixing and releasing radionuclides in gypsum stack environments are discussed in Chapters 3 and 4 of this report.

The finest-grained water insoluble residues contain the highest activities of ^{210}Pb and ^{226}Ra and the possibility that this fine-grained, organic material contains a proportion of the radioactivity in phosphogypsum was investigated even though the first sequential leaching experiments with H_2O_2 did not liberate appreciably higher activities of ^{226}Ra to solution and there is no discernible relationship of ^{226}Ra in solution with dissolved organic carbon. Three replicate samples of Gyp-46 insoluble residues were analyzed for total organic carbon (TOC) and nitrogen (N) because of the high proportion of ^{226}Ra that Gyp-46 releases into DDW solutions. Results are presented in Table 2-27 and TOC ranges from about 6 - 8% of the total mass of the finest-grained residue and nitrogen (N) is negligible. Carbon is present, but the role it plays in the sorption of radionuclides is still not clear. Sorption of radionuclides onto carbon in the gypsum stack environments may not be a viable process because of the low pH of solutions would tend to inhibit sorption and the high chemical activity of calcium and calcium complexes would be expected to occupy most of the sorption sites. The same may be true for radionuclide sorption onto calcium sulfate complexes, but these processes can not be evaluated until the solutions which are circulating in the gypsum stacks can be better characterized.

Multicomponent Chemical Equilibrium Models

Both homogeneous (SOLVEQ) and heterogeneous (CHILLER) chemical equilibrium models predicted that barite ($BaSO_4$) and strontianite ($SrSO_4$) would be highly insoluble in solutions that were produced during dissolution of phosphogypsum with DDW using the solvent/solute ratio (25 g of phosphogypsum dissolved in 18 L of DDW) used in all of the "D" series dissolution experiments. The chemical composition of Gyp DL3 was used in these models and the composition was normalized to a dihydrate form (gypsum) which was know to be the predominant phase present from XRD of the bulk samples. Anglesite ($PbSO_4$) should also be insoluble in these solutions, at least in theory, if the pH does not decrease below about 2.7. The pH measured in supernatant solutions for 3 "D" series dissolutions of Gyp DL3 never decreased below about 3.6.

No internally consistent thermodynamic data exist for a (Ba,Sr,Pb)SO4 type of mineral phase that has been postulated as being present in phosphogypsum or the $(Ca,Sr,Ba)SO_4$ phase mentioned by Moisset (1990) as the probable site of ^{226}Ra in fine-grained residues that were produced by dissolving and hydrocycloning HH. However, CHILLER models of the majority of the water insoluble residues of Gyp-46 and Gyp DL3 indicated that the sulfate (SO_4^{2-}) that remained in the residues after all the DH was dissolved was insufficient to balance all of the Ba as barite. A solid solution phase such as $(Ba,Sr,Pb)SO_4$ or $(Ca,Sr,Ba)SO_4$ would therefore be even less likely to be present since a higher molality of sulfate would be required to precipitate all of the Ba, Sr, and Pb. Based on our compositional data, it is unlikely that all of the ^{226}Ra or ^{210}Pb could be co-precipitated as divalent sulfates. A neutrally-charged aqueous species of radium, $RaSO_4^{\circ}(aq)$ was calculated in SOLVEQ models of the "D" series type dissolutions of Gyp

Table 2-27. Percentages by mass of C and N in replicate samples of three sub-samples of the finest-grained, $CaSO_4 \cdot 2H_2O$-free, water-insoluble residues from Gyp-46 dissolution D3. This residue was X-rayed to assure that no $CaSO_4 \cdot 2H_2O$ and very little quartz was present in this residue.

Sample Name	C % by Mass	N % by Mass
Gyp-46 D3 O1A	8.051	0.043
Gyp-46 D3 O1B	6.011	0.060
Gyp-46 D3 O2A	6.262	0.049
GYP-46 D3 O2B	6.531	0.056
Gyp-46 D3 O3A	6.482	0.058
Gyp-46 D3 O3B	6.276	0.078

DL3, but the molality was extremely low. However, not much radium in solution would be required to account for the activities of ^{226}Ra that we have measured in solutions.

Rare earth fluorides (LaF_3 and CeF_3) were not modeled using the numerical modeling techniques because the chemical thermodynamic data for these phases are not contained in the database as yet. Fluorite (CaF_2) was saturated in some CHILLER models of solutions that had the same solute/solvent ratios of the "D" series solutions and surprisingly so was topaz [$Al_2(SiO_4)(OH,F)_2$] which has been synthesized by heating amorphous Al_2O_3 with Na_2SiF_6 (Deer et al., 1966). This silica hexafluoride phase is the Na end-member of the solid solution phase that we have identified growing in seeps of discharge fluids in gypsum stacks and is well know to analytical chemists and production managers in the fertilizer industry as the mineral phase that clogs filter screens. This coincidence is even stranger considering that gypsum stacks and filter pans in phosphoric acid plants are the only places, with the exception of high temperature volcanic vents, this mineral phase has been identified. We have measured the activities of radionuclides in crystals of $(K,Na)_2SiF_6$ collected on gypsum stacks and activities of ^{226}Ra and ^{210}Pb are near the lower limits of detection. The relevance of this information to this study is that all of these mineral phases, with the exception of the $(K,Na)_2SiF_6$ based on our data, are capable of scavenging radionuclides from solutions. In fact, co-precipitation of radionuclides from solutions with rare-earth element fluorides, as CeF_3, is a standard practice in radiochemistry laboratories.

CONCLUSIONS

Based on the observations made in this chapter, we summarize the principal conclusions below.

(1) A radionuclide-enriched fraction of bulk phosphogypsum samples cannot be produced, at least on a laboratory scale, by either standard dry or wet sieving techniques. It may be worth investigating more sophisticated sieving techniques which utilize surfactants and/or ultrasonic vibration during the processing and filtering of the solids.

(2) Neither ^{226}Ra nor ^{210}Pb were released in direct proportion to $CaSO_4 \cdot nH_2O$ dissolution in DDW. The fractionation between ^{226}Ra and ^{210}Pb implies that these radionuclides either exist in phosphogypsum as different phases or display different adsorption characteristics.

(3) Both ^{226}Ra and ^{210}Pb are enriched in water-insoluble solid residues after $CaSO_4 \cdot nH_2O$ has been completely dissolved. The great majority of radium is adsorbed or is included within a discrete phase rather than being incorporated as lattice component in the $CaSO_4 \cdot nH_2O$ crystals.

(4) Supernatant solutions produced by dissolving bulk phosphogypsum samples in DDW released appreciable portions of ^{226}Ra to solution when virtually all the $CaSO_4 \cdot nH_2O$ phase in bulk samples was dissolved. Although a significant portion of ^{226}Ra is apparently in solution as defined by the ability to pass through a 0.45 μm filter, radionuclide incorporation onto colloids cannot be ruled out. The release of ^{226}Ra into solution does not seem to be an obvious function of the time phosphogypsum has been on a storage stack.

(5) The great majority of radionuclides in water insoluble residues of phosphogypsum are contained by the finest-grained material. The activities of ^{210}Pb retained by these finest-grained residues are about twice as high as activities of ^{226}Ra. Thus, ^{226}Ra is apparently more easily desorbed/leached from the solid phases which contain the majority of the radionuclides.

(6) Heavy liquid separations of water insoluble residues of phosphogypsum samples were not successful in isolating a radionuclide-enriched fraction of the insoluble residues.

(7) Radionuclides in phosphogypsum are not strongly bound by organic material. There does not appear to be any relationship between the concentration of dissolved organic carbon and the activities of ^{226}Ra in solution.

(8) Quartz and cryptocrystalline apatite were detected in every water-insoluble residue of phosphogypsum that was been analyzed by XRD. Aluminum phosphates and complex calcium and iron aluminophosphates were identified by XRD in some of the finest-grained residues when all the $CaSO_4 \cdot nH_2O$ was dissolved and most of the quartz was removed.

(9) No Ba or Sr has been detected in semiquantitative XRF analyses of fine-grained, water insoluble residues of phosphogypsum. We did observe small nodular materials with high contents of Al, Si, Ca, and Fe. This could be due to the presence of chukhrovite ($Ca_4SO_4SiAlF_{13} \cdot nH_20$) which was identified by XRD in water-insoluble residues of phosphogypsum.

(10) Barite does <u>not</u> contain the majority of ^{226}Ra in phosphogypsum. It appears that most of the insoluble ^{226}Ra and ^{210}Pb in phosphogypsum may be associated with an aluminum-rich phase. Complex iron phosphates and calcium alumina phosphates may also contain portions of the radionuclides. The main radionuclide carrier phase may have a composition similar to the mineral crandallite, $CaAl_3(PO_4)_2(OH)_5 \cdot H_2O$. Fluoride phases, specifically CeF_3 and LaF_3 may also host significant portions of the radionuclides in phosphogypsum matrices.

CHAPTER 3

UPTAKE OF POLONIUM AND SULFUR BY BACTERIA

INTRODUCTION

Polonium-210 is the final alpha-emitting daughter nuclide in the natural uranium-238 decay series. It normally is considered a "particle reactive" element (tends to adsorb to negatively charged particles) and as such has been used as a tracer to study the mechanisms of metal removal by particles in aquatic systems (Talbot and Andren, 1984; Benoit and Hemond, 1987; Harada *et al.*, 1989). Ranked in the very hazardous group of radionuclides, polonium is considered to be extremely radiotoxic when ingested. The maximum contaminant level for natural gross alpha-particle activity in drinking water is 15 pCi/L, as defined by the U.S. Environmental Protection Agency (Aieta et al., 1987). Some groundwaters from shallow wells in west-central Florida, however, were found to have ^{210}Po activities greater than 500 pCi/L (Burnett *et al.*, 1987; Harada *et al.*, 1989). The exact source of Po in these wells is uncertain although it must somehow ultimately be related to the relatively high content of uranium (~100 ppm) and subsequent daughter products found naturally in phosphatic strata characteristic of the region. Phosphogypsum ($CaSO_4 \cdot 2H_2O$ with impurities) is another potential source of polonium found in ground waters in this area. It is a by-product formed during the chemical processing of phosphate rock where concentrated ore is reacted with sulfuric acid to produce phosphoric acid, the raw material used for production of phosphatic fertilizers. Because of its relatively high content of radionuclides, phosphogypsum is not used commercially and currently is being stockpiled at a rate of several tens of millions of metric tons per year.

A detailed study of one well with ^{210}Po activities consistently over 500 pCi/L

showed that virtually all of the ^{210}Po in the sampled wells was unsupported; *i.e.*, its presence was unaccompanied by its radioactive predecessors ^{210}Pb and ^{210}Bi (Harada *et al.*, 1989). Some process, therefore, must be affecting the geochemistry of Po such that it is capable of migrating and concentrating in the ground water system. Furthermore, evidence presented by these authors led them to suggest that soluble Po was preferentially released from the surrounding phosphate rock by indigenous microorganisms. They showed that ground waters with high ^{210}Po concentrations were also characterized by the presence of sulfide at levels greater than approximately 10μM H_2S, and pH values generally lower than 5. Harada and his colleagues also experimentally investigated the relationships between bacterial growth, Po activity, and sulfide concentrations in Po-rich ground water. They observed a concurrent increase in bacterial biomass and particulate Po and an equivalent decrease in soluble Po and sulfide over a time scale of hours to days. These findings suggested that bacterial activity and uptake of soluble Po in ground water could be a dominant factor controlling the distribution between soluble and particulate phases. Because Po and sulfur have some chemical affinities (both elements, for example, are members of Group VI in the periodic table) and the absolute maximum chemical concentrations of Po in the study site wells were too low (approximately $10^{-16}M$) to serve in any direct metabolic function, it was hypothesized that biochemical mechanisms governing sulfur metabolism could also affect the uptake and cellular distribution of polonium in the indigenous bacterial populations.

Sulfur can enter into bacterial metabolism in three ways: (1) as an energy source (sulfide oxidation); (2) as a terminal electron acceptor (dissimilatory sulfate reduction); or (3) as a precursor for the synthesis of the amino acids cysteine and methionine (assimilatory sulfate reduction). In suboxic marine waters, Cutter (1982) and Cutter and Bruland (1984) have demonstrated the existence of a reduced form of the element selenium (another Group VI element) which they operationally-defined as organic selenide. They found that most of this organic selenide was associated with dissolved amino acids and suggested that it might exist as selenocysteine and selenomethionine. In terms of polonium behavior in natural waters, the most common valance state is thought to be Po^{4+} (Bacon et al., 1988). Bagnall(1957), however, noted that while the reduced form of Po, H_2Po, has never been isolated in weighable amounts, there is tracer scale evidence for its formation. These observations led us to speculate that Po might be reduced in a similar manner as sulfur in the normal course of microbial metabolism (*i.e.*, assimilatory sulfate reduction) to form Po-labeled proteins.

The long-term goal of our research concerning polonium-bacteria interactions is to determine if bacterial activity is central to the mobilization of Po from the solid phase to the fluid portion of the aquifer. Earlier studies in our laboratory (Harada *et al.*, 1989) provided circumstantial evidence for polonium uptake by bacteria after Po-enriched ground waters had been removed from the

aquifer. The experiments reported here were designed to evaluate the mechanisms and fate of polonium after uptake. Another report (see Chapter 4) will deal with the specific issue of bacterial mobilization of polonium from phosphogypsum. In this report, we compare the patterns of uptake and cellular compartmentalization of Po and sulfur using a bacterial culture isolated from a freshly-collected phosphogypsum sample. The results indicate that while the initial mechanism of bacterial uptake for SO_4 and Po appears to differ, once Po is associated with the cell, it is dispersed between the cell walls, cytoplasm, and protein in a manner very analogous to sulfur. These observations thus serve to establish that bacteria may, in fact, be involved in the "processing" of aqueous polonium species.

MATERIALS AND METHODS

Organism. Culture Media. and Radioisotopes

The aerobic bacterial culture used in all experiments was isolated on nutrient agar (Difco Laboratories, Inc., Detroit, Mich.) from a phosphogypsum sample collected from an inactive gypsum stack (IMC P-21 stack) in Bartow, Florida. The Gram negative rod-shaped cells were classified in the *Psuedomonas* group using Biolog Microplates™ (Biolog, Inc., Hayward CA). The isolate was maintained on the low-nutrient medium described below. All experiments employed a nutrient medium that consisted of 0.08% peptone, 0.02% yeast extract (Difco Laboratories, Inc.), 1 mL of trace metals solution, basal salts, and distilled water. The basal salts per liter of medium were as follows: 0.02g Na_2SO_4, 0.10g KH_2PO_4, 0.25g NH_4Cl, 1.0g NaCl, 0.40g $MgCl_2 \cdot 6H_2O$, 0.50g KCl, and $CaCl_2 \cdot 2H_2O$. The trace metals stock solution (1,000 fold concentrated) consisted of the following compounds per liter of distilled water: 8.5 mL of concentrated HCl, 2.1g of $FeSO_4 \cdot 7H_2O$, 0.10g $MnCl_2 \cdot 4H_2O$, 0.19g $CoCl_2 \cdot 6H_2O$, 0.144g $ZnSO_4 \cdot 7H_2O$, 0.006g H_3BO_3, 0.024g $NiCl_2 \cdot 6H_2O$, 0.002g $CuCl_2 \cdot 2H_2O$, and 0.036g $Na_2MoO \cdot 2H_2O$.

We omitted Na_2SO_4 from the medium for those experiments in which sulfate partitioning was examined, relying only on the sulfate-S contained in the peptone and yeast extract to support growth. The non-labeled sulfate-S concentration in the medium for these experiments was 1.7mg SO_4-S L^{-1} as measured with a Dionex 4500i Ion Chromatograph, equipped with an ASHA anion exchange column.

To compare how bacteria use sulfur and polonium, we employed commercially-available radioisotopes of sulfate ($Na_2{}^{35}SO_4$, 5.0mCi/mL, NEN, DuPont Biochemicals, Boston, MA) and polonium ($^{208}PoCl_4$, 0.5µCi/mL, Isotope Products Laboratories, Burbank, CA). The bacteria were grown in 250 mL of

medium to which a total activity of either $^{35}SO_4$ (6.0µCi) or ^{208}Po (0.028µCi) had been added. Cost considerations dictated that initial isotopic concentrations of the medium in the growth flasks labeled with ^{208}Po be much lower than those labeled with $^{35}SO_4$. Even at trace concentrations, polonium is known to bind to charged surfaces and exhibit colloidal behavior (Bagnall, 1957). In an effort to minimize losses of polonium to glass-ware, we used only plastic growth vessels, centrifuge tubes, spectrophotometer cuvettes, and filtration units.

Changes in optical density were used to follow bacterial development in growth experiments and to determine the physiological phase of the culture. Absorbance readings (OD_{610}) were calibrated against direct cell counts by phase contrast microscopy using a Petroff-Hauser cell so that optical density could be used to subsequently determine cell numbers when required.

Polonium and Sulfate Incorporation Experiments

The respective radiolabled growth media *(i.e.,* $^{35}SO_4$ or ^{208}Po) were inoculated with approximately 9.0 x 10^4 cells, placed on a shaker table, and allowed to incubate at room temperature (23°C) for periods up to 90 hours. At selected time intervals within the bacterial growth cycle, 10 mL aliquots were removed from each culture flask to (1) measure changes in optical density, and (2) determine total cellular uptake of the appropriate radioisotope. These aliquots were passed through a 0.3 µm membrane filter (Millipore Corp., Bedford Ma). The filter was washed twice with sterile distilled water and then counted by liquid scintillation (LSC) to measure cell-associated radioactivity. The filtrate (1 mL aliquot) was also counted to quantify the isotope not taken up by the bacteria in order to conduct a mass balance of the isotope between the culture media and the bacteria. Filter backgrounds for each isotope were determined by filtering cell-free labeled media through a membrane filter, as was done for the samples themselves, and subtracting the measured background from sample counts. Total isotope uptake and culture growth were expressed as net counts per minute (cpm) and optical density (OD), respectively. The experimental procedures for the isotope incorporation as well as the fractionation experiments are outlined in the accompanying flow chart (**Figure 3-1**).

Cellular Partitioning of Polonium And Sulfur

The partitioning of Po and SO_4 within the bacterial culture was determined by fractionating the cells using a modification of the methods of Schneider (1945; 1946), Burrous and Wood (1962), and Gray and Thurman (1967). At various stages during the growth cycle, cells in 10 mL subsamples were harvested by centrifugation (4500 x g for 30 minutes at 4°C) and washed once in a 0.85% NaCl-1 mM EDTA solution. The cells were resuspended in 5 mL tris buffer (pH 7.8) and lysed with lysozyme (10 mg/mL, Sigma Chemical Co., L6876, St Louis, MO) and a

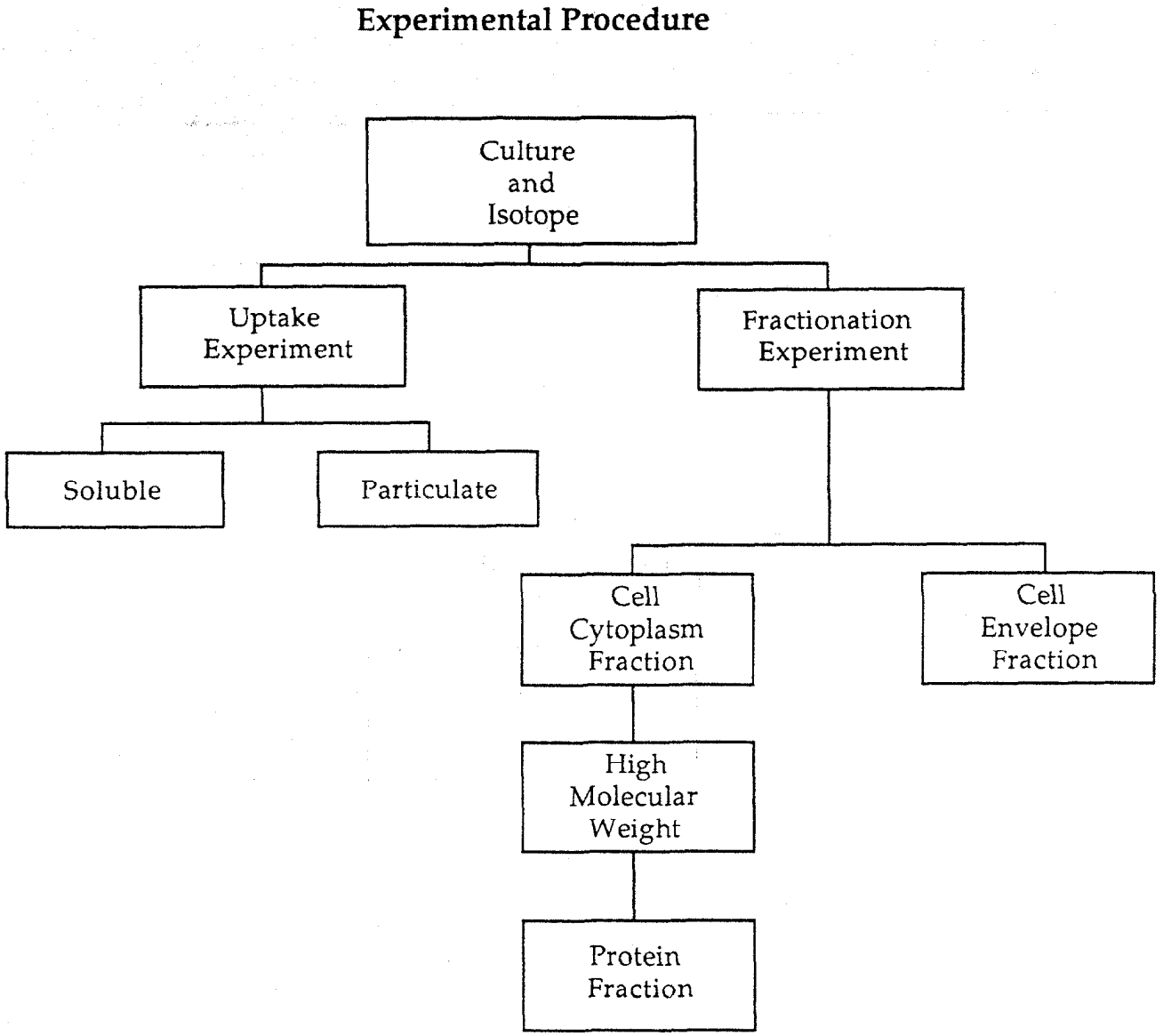

Fig. 3-1. Flow chart of the experimental procedures for Po and SO_4 uptake and fractionation experiments.

10% sodium lauryl sulfate detergent solution. Once lysed, the suspension was centrifuged (40,000 x g for 30 minutes at 4°C) to pellet the cell envelope, and the supernatant containing the total cell cytoplasm was saved for further analysis. The cell envelope (pellet) and a 1 mL aliquot of the cell cytoplasm were counted for total radioactivity. The remaining cytoplasmic material was fractionated to isolate proteins and nucleic acids to determine how the radiotracer was partitioned intracellularly.

The high molecular weight (HMW) compounds, which include the nucleic acids and proteins, were collected by cold 10% trichloroacetic acid (TCA) precipitation from the cytoplasmic fraction. These then were washed with ethanol and counted by LSC. The separation of nucleic acids from protein was done on duplicate samples, which were further processed by resuspending the HMW precipitate in 5% TCA and heating it for 15 minutes at 90°C to dissolve the nucleic acids and leave the insoluble protein precipitates behind. This precipitate was then collected by centrifugation, washed in ethanol, and the activity measured by LSC.

Experimental Controls

The inhibition of the production of bacterial proteins by the addition of chloramphenicol was chosen as an experimental control. Chloramphenicol blocks protein synthesis by inhibiting peptide chain elongation. A 150 mg/L solution was added to growth flasks at the middle of the log phase (approximately 16th hour of growth) and the culture incubated for another hour, after which radiotracer was added to the respective flasks. The chloramphenicol-treated samples were analyzed for uptake and isotope fractionation along with the experimental cultures as detailed above. All uptake and fractionation experiments, together with their respective controls, were run in duplicate and the results averaged. The average coefficient of variation between duplicate samples for $^{35}SO_4$ and ^{208}Po were 0.18 and 0.11, respectively.

RESULTS AND DISCUSSION

We conducted comparative radioisotope uptake and cellular fractionation experiments to determine if polonium behaved similarly to sulfur and entered into the bacterial metabolic cycle. Theoretically, both isotopes could be reduced and incorporated into bacterial proteins if Po does mimic sulfur. However, this simple model may be complicated by two factors. First, Po^{4+} differs from the SO_4^{2-} molecule in its overall charge and consequently its reactivity in solution. Polonium is highly surface reactive and in trace concentrations will adsorb onto any negatively charged surface (Bagnall, 1957), whereas $^{35}SO_4$ will not. This difference in the adsorptive quality of polonium presents an alternate mechanism (*i.e.*, passive adsorption) by which it may be removed from the

solution. Secondly, the chemical concentration of Po in the growth medium was orders of magnitude lower (10^{-14}M) than the sulfate concentration (1.7 x 10^{-4}M), and thus our experiments were restricted to a comparison of the patterns of isotopic uptake and cellular partitioning of the two elements.

Polonium and Sulfate Incorporation Experiments

At selected intervals within the bacterial growth cycle subsamples of labeled culture (either $^{35}SO_4$ or ^{208}Po) were filtered to determine the temporal changes in isotope uptake by the bacteria **(Figure 3-2).** Four percent of the total $^{35}SO_4$ available in the medium was associated with the cells by the onset of the stationary phase (Fig. 3-2a). A mass balance of the cell-associated ^{208}Po (filter) and the ^{208}Po remaining in solution (filtrate) indicated that approximately 35% of the ^{208}Po added to the culture medium was unaccounted for and presumably lost to adsorption onto the growth flask. However, of the ^{208}Po remaining in solution, 96% was cell associated by the late log phase (OD=0.4 in Fig. 3-2b). The shapes of the isotope uptake and optical density curves revealed that incorporation essentially paralleled culture growth for sulfate (Fig. 3-2a), whereas Po. incorporation (Fig. 3-2b) preceded exponential growth and 50% of the available Po had been removed from solution by the early log phase (O.D.=0.15).

This difference in incorporation patterns between SO_4 and Po can be seen more clearly by plotting the cell-associated radioactivity against bacterial numbers (**Figure 3-3**). There is a direct relationship between the number of cells in the culture and the quantity of ^{35}S retained by the bacteria. Uptake of SO_4 was directly proportional to cell number during both the lag and exponential growth phases. Polonium, however, behaved very differently. Polonium displayed two apparent rates with uptake more rapid during the late lag phase (slope=2.4) and slower during exponential growth (slope=0.7). At low cell numbers (Log Cell No=7.5-7.8, in Fig. 3-3) Po was scavenged from solution until approximately 50% of the PO had been removed and was associated with the bacteria. As the culture grew the rate of the Po removal declined, reflecting almost complete depletion of the element from the growth medium.

The differences in Po uptake rate can be explained on the basis of the element's surface reactivity and the negative charge associated with the bacterial cell wall. The cell walls of gram negative bacteria are characterized by a high lipid content which, when the pH is greater than 4, imparts a negative charge to the bacterial surface (Lamanna and Mallette, 1965; Richmond and Fisher, 1973; Doyle *et al.*, 1980; Urrutia *et al.*, 1992). As the number of bacteria in the culture begin to increase, they provide negatively charged surfaces that will preferentially scavenge Po until it is totally removed from solution. The interaction between Po and bacteria appears to be a two-step process in which Po is first adsorbed onto the cell surface, and then (as will be shown later) processed

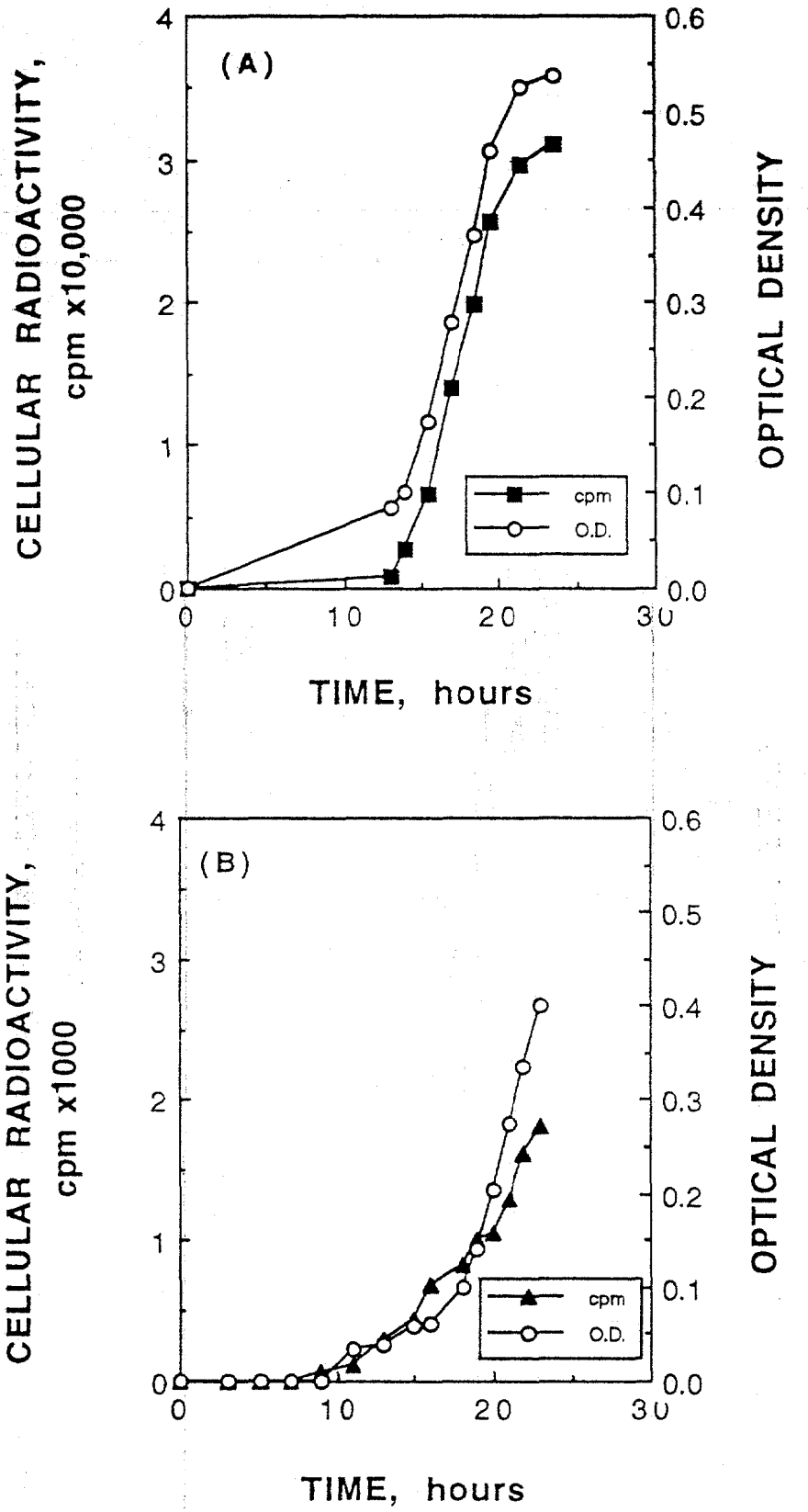

Fig. 3-2. Isotope uptake and culture growth shown for SO_4 (A) and Po (B) uptake experiments.

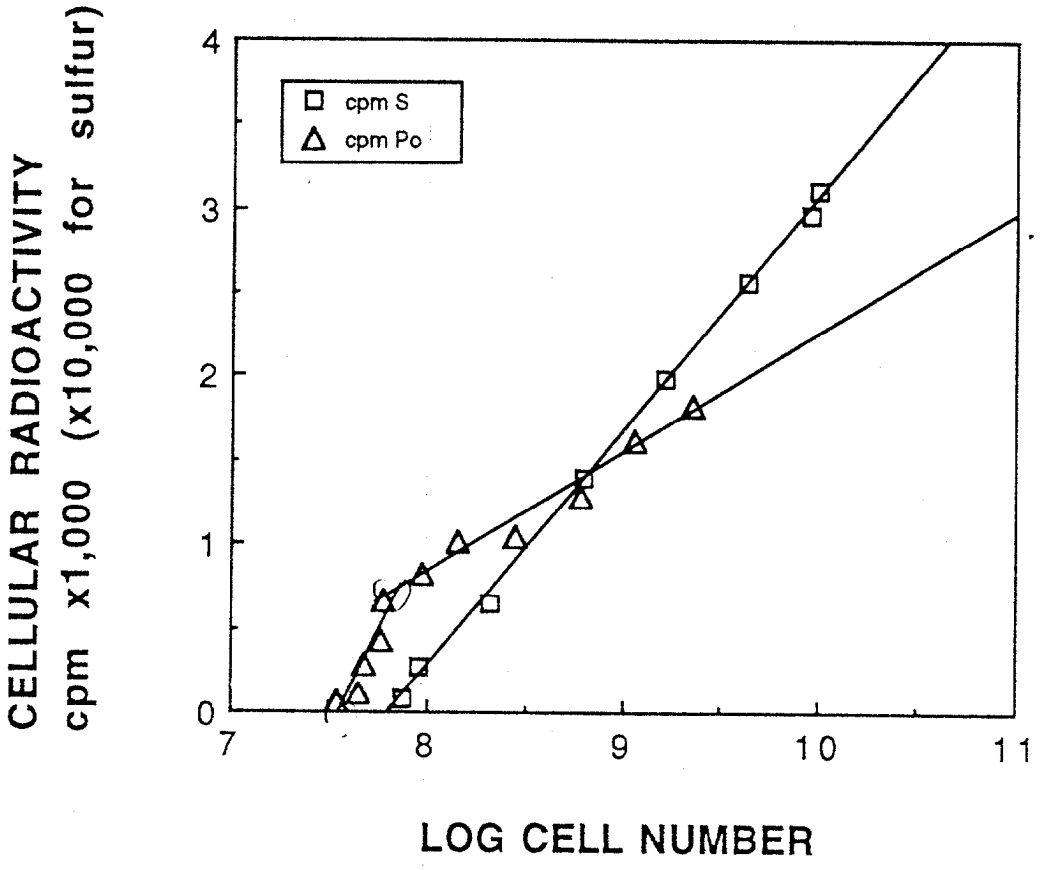

Fig. 3-3. Cellular radioactivity of ^{208}Po and ^{35}S plotted against cell number.

internally by the organism.

The question now arises as to whether Po is processed further by the cell for protein synthesis as is the case for sulfate. Uptake and incorporation of Po by marine microbiota (*i.e.*, bacteria and algae) have been reported for oceanic systems, although the mechanisms involved are not well understood (Fisher *et al.*, 1983; Heyraud and Cherry, 1983; Bacon *et al.*, 1988). Fisher *et al.,* (1983) investigated the relationship between marine algae and polonium and noted that while Po may initially adsorb to cell surfaces, the relatively uniform distribution of Po in various cell fractions was reflective of eventual cellular incorporation.

In order to assess the possibility of Po incorporation into cellular proteins we added chloramphenicol to control samples during early exponential growth (hour 16, in **Figure 3-4)** to block protein synthesis and then followed its effect on culture growth and isotope uptake **(Figure 3-5).** Culture growth was negligible following the addition of chloramphenicol (Fig. 3-4). The OD in control flasks increased from 0.16 to 0.20, reflecting approximately one population doubling, as compared to the experimental sample increase of 0.15 to 0.45 (more than 4 population generations). The addition of chloramphenicol surpressed SO_4 uptake and curtailed culture growth (final OD=0.28 in Fig. 3-5a compared to an OD=0.45 in Fig. 3-4 for untreated samples) as is reflective of blocked protein synthesis. Only 0.17% of the total available SO_4 was taken up by cells in the control flasks as compared to 4% in the experimental flasks. In sharp contrast to SO_4, Po uptake by the chloramphenicol treated culture continued to the point where 58% of the polonium in solution was associated with cells by 22 hr and 71% after 24 hr (Fig. 3-5b). The distinctly different effects of chloramphenicol on SO_4 and Po uptake further supports our hypothesis of a two-step mechanism for PO removal from solution, namely Po scavenging by negatively-charged bacteria followed by physiological processing.

Cellular Partitioning of Polonium and Sulfate

Cells were fractionated into their various cellular components to (1) determine where the cell-associated polonium ultimately resides, *i.e.*, cell envelope, cell cytoplasm, or cell proteins; and (2) determine how the patterns of polonium incorporation compared to that of sulfur. Since sulfur is a constituent of the amino acids cysteine and methionine and is primarily incorporated into cell proteins, it was hypothesized that bacterial cometabolization of polonium with sulfur would result in a similar intracellular cell distribution for $^{35}SO_4$ and ^{208}Po with a fraction of each isotope associated with cell proteins. Alternatively, if polonium uptake was the exclusive result of passive adsorption to the bacterial surfaces then the majority of the isotope would be expected to be found in the cell envelope fraction.

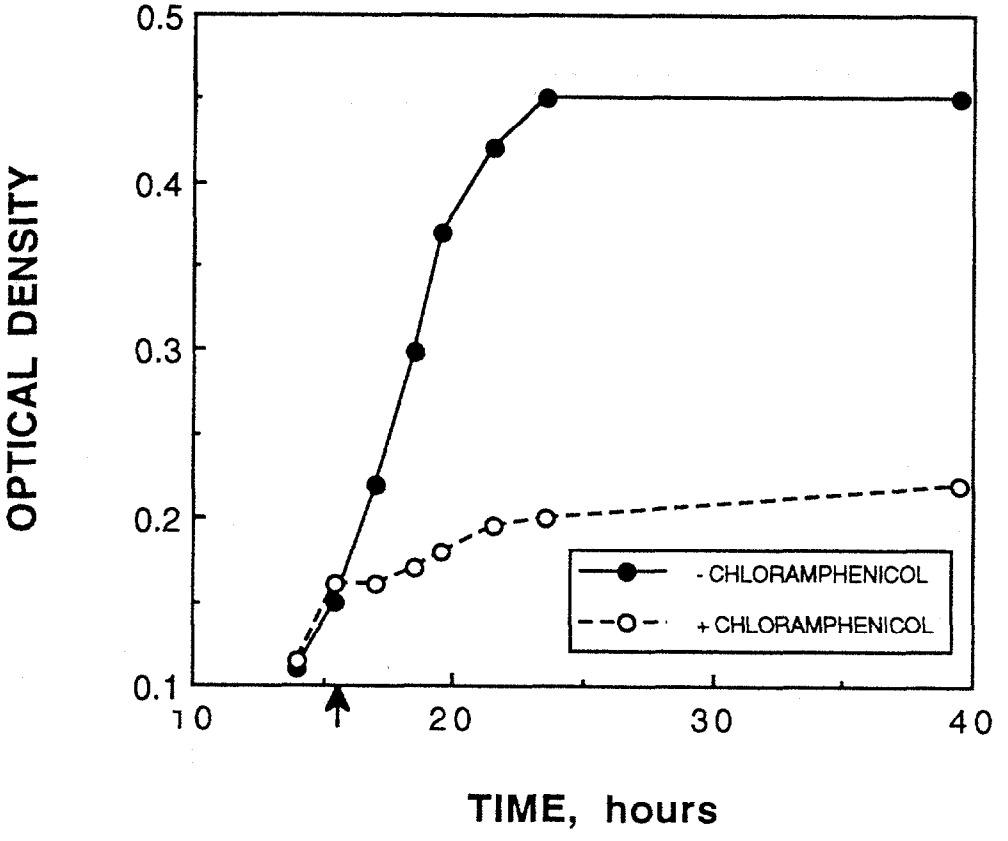

Fig. 3-4. Culture growth shown for both normal experimental conditions and with the addition of chloramphenicol (time of addition shown by arrow).

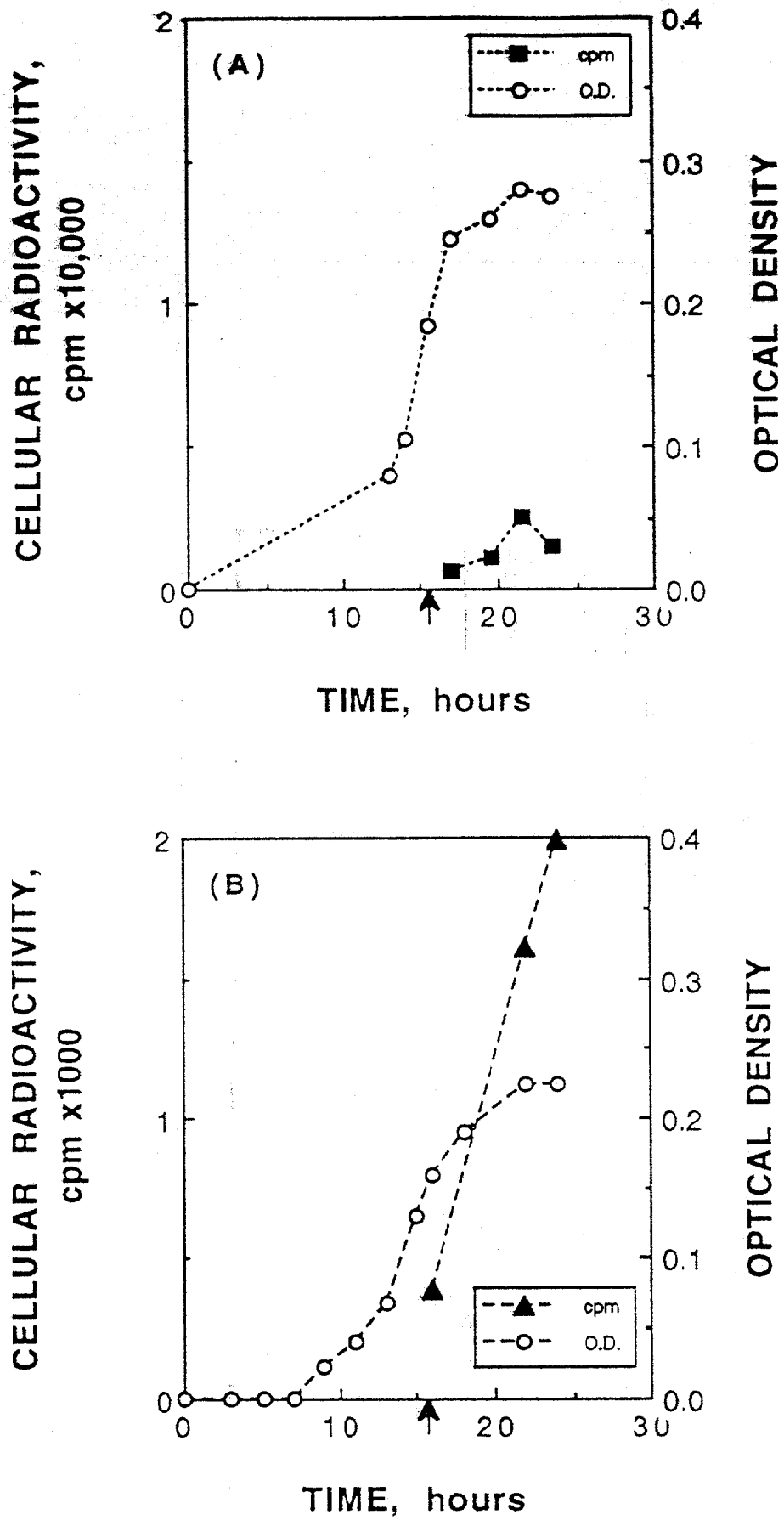

Fig. 3-5. Isotope uptake and culture growth shown for SO_4 (A) and Po (B) in chloramphenicol-treated control samples.

At selected time intervals within the bacterial growth cycle, aliquots of the labeled culture (either SO_4 or Po) were removed and the cells fractionated into (1) cell envelope, (2) cell cytoplasm, (3) a high molecular weight fraction consisting of nucleic acids and proteins, and (4) the protein fraction alone. The experimental procedure dictated that first both nucleic acids and proteins be jointly separated from the cytoplasmic material. However, no statistical differences for the activities of the HMW fraction and the protein fraction ($p=.433$, Wilcoxon Rank Sum Test) were found. This was not surprising since sulfur is not a component of nucleic acids. Hence, the data from the HMW and protein fractions were pooled, averaged, and expressed cumulatively as the "protein fraction" since proteins (not nucleic acids) were the presumed cell target for both SO_4 and Po. Also, because proteins were extracted from the cell cytoplasm, that activity associated with the proteins has been accounted for and the activity in the cytoplasm has been expressed as cytoplasm less the cell proteins.

The cellular distribution of SO_4 and Po in late stationary phase cells (hour 40) has been summarized in **Table 3-1** for both experimental and chloramphenicol treated controls. Although the total cellular radioactivity of experimental samples was more than ten times greater for SO_4 labeled cells (28,600 cpm) than for the cells labeled with Po (2250 cpm), the cellular partitioning patterns were similar for both isotopes **(Figure 3-6**, Table 3-1). In the experimental samples both sulfur and polonium were approximately evenly distributed between the cell envelope (46% SO_4, 47% Po) and the cytoplasm (49% SO_4, 40% Po) with a small fraction associated with the cell proteins (5% SO_4, 13% Po).

The chloramphenicol treated samples also exhibited similar distribution patterns for SO_4 and Po (Fig. 3-6b) even though the uptake for each isotope was dramatically different *(i.e.,* SO_4 uptake essentially ceased but Po uptake continued, Fig. 3-5). In the control samples, SO_4 and Po were associated almost exclusively with the cytoplasm (88% SO4, 85% Po) and very little isotope associated with either the cell envelope (0.01% SO_4, 6% Po) or the protein fractions (11% SO_4, 7% Po). While chloramphenicol blocked polypeptide formation, it is possible that the viable cells (see Fig. 3-4) were still capable of taking up and storing protein precursors in cytoplasmic pools in an attempt to synthesize proteins (Gottlieb and Shaw, 1967). It was therefore not surprising that the label (either $^{35}SO_4$ or ^{208}Po) in the control samples was predominantly associated with cell cytoplasm. Another important point to note is that after chloramphenicol was added to the control samples, the cultures went through one additional doubling before cell growth was inhibited (Fig. 3-4). This could explain why a small fraction of isotope was found associated with the cell proteins in both $^{35}SO_4$ and ^{208}Po controls. Of primary significance, however, was

TABLE 3-1 Cellular partitioning of $^{35}SO_4$ and ^{208}Po in stationary phase cultures.

Isotope/ treatment	Cell number analyzed	Total cellular radioactivity (cpm)	Envelope activity cpm ± s.d.	% total	Cytoplasm[a] activity cpm ± s.d.	% total	Protein activity cpm ± s.d.	% total
$^{35}SO_4$ (EXP[b])	5.90E+09	28,610	13,300 ± 2000	46%	13,900 ± 1020	49%	1,410 ± 290	5%
$^{35}SO_4$ (CON[c])	3.40E+08	2,040	30 ± 20	1%	1,780 ± 270	88%	230 ± 90	11%
^{208}Po (EXP[b])	1.20E+10	2,250	1,050 ± 220	47%	900 ± 220	40%	300 ± 120	13%
^{208}Po (CON[c])	7.10E+08	2,180	130 ± 30	6%	1,890 ± 90	85%	160 ± 149	7%

[a] cytoplasm less protein fraction

[b] experimental sample

[c] control sample

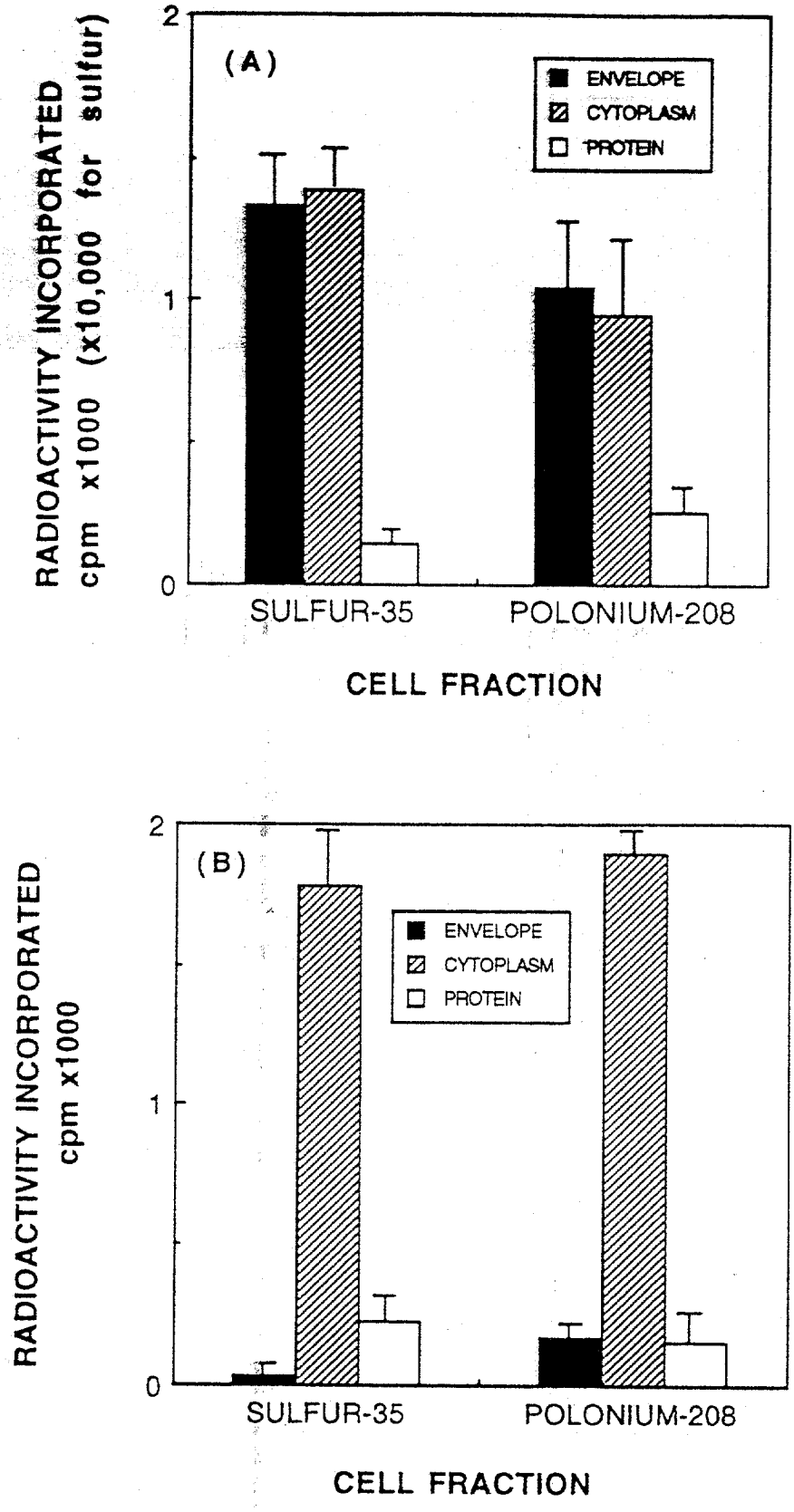

Fig. 3-6. Cellular distribution patterns of SO_4 and Po for: (A) experimental; and (B) chloramphenicol-treated samples taken during the late stationary phase of culture growth. Error bars represent the standard deviation from the mean between duplicate samples.

that the cellular distribution patterns of both $^{35}SO_4$ and ^{208}Po were similar to each other in all treatments even though there were dramatic differences in the cellular partitioning between the experimental and chloramphenicol-amended samples.

SUMMARY

The findings reported here suggest that although the initial uptake mechanisms of sulfur and polonium may differ (Figs. 3-2, 3-3, and 3-5), similar mechanisms appear to govern their fate within bacterial cells. Whether or not sulfur and polonium are cometabolized has not been resolved by these experiments. The similarity in the partitioning patterns of $^{35}SO_4$ and ^{208}Po, however, does suggest that polonium may undergo assimilatory reductive reactions similar to those of sulfur. This implies that Po could be reduced in dissimilatory processes and could explain, for example, how Po is mobilized from phosphate rock or phosphogypsum and occasionally attains the high groundwater concentrations such as are found in parts of west central Florida. In addition, the uptake experiments reported here show that bacteria may be very effective in removing Po from aqueous solutions. This opens the possibility that a bioremediation scheme could be devised for Po decontamination of domestic or process waters.

CHAPTER 4

BACTERIAL MOBILIZATION OF POLONIUM

INTRODUCTION

High levels of alpha-emitting radionuclides of the uranium decay series in central Florida groundwater taken from the surficial aquifer have been reported (Burnett *et al*., 1987). Of particular interest was the finding that in some areas ^{210}Po accounted for virtually all of the activity in the complete absence of its radiogenic predecessors ^{210}Pb and ^{210}Bi. Levels of 1,000 dpm/l or more have been reported, in contrast to the few dpm that are ordinarily encountered in most radiochemical surveys (Krishnaswami *et al*., 1982; Hess *et al*., 1985). Polonium is the last member of the ^{238}U decay series and is produced from the decay of ^{210}Pb *via* ^{210}Bi. Little is known about Po geochemistry other than that the element has two oxidation states (+2 and +4) and that it will react with sulfide to form PoS_2 (Bagnall, 1957). Polonium is also particle-reactive, a property that has been used to study removal mechanisms of metals in lakes and seawater. Reports dealing with Po in seawater systems indicated that $^{210}Po/^{210}Pb$ range from about 0.2 to 1 and that the ratio appeared to be affected by biological productivity and upwelling (Harada *et al*., 1989).

In previous experiments (Harada *et al*., 1989), we demonstrated that Po loss from a ground water sample paralleled the growth of the microbial consortium in that sample and that Po appeared in the particulate phase as it was removed from solution. Sulfide also was lost, and the implication was that sulfide oxidizing bacteria affected the loss of both sulfide and Po. The simultaneous occurrence of sulfide and Po in groundwater, the concurrent removal of both by bacteria under aerobic conditions, and the fact that Po and sulfide may behave in a chemically similar manner (both are in the same column in the periodic table) suggested that factors affecting sulfur cycling could also affect Po availability.

The uranium-containing phosphorite deposits in central Florida serve as the raw material for the manufacture of fertilizers and phosphoric acid, obtained by treating phosphate rock with sulfuric acid. Consequently, the single largest regional source of sulfur in central Florida is the sulfate which is tied up in phosphogypsum, a by product of phosphoric acid manufacture. There is currently over 600 million metric tons of phosphogypsum in Florida with another 30-40 million tons being added each year. All this material is stockpiled because the relatively high content of radionuclides (primarily ^{226}Ra, ^{210}Pb, and ^{210}Po) and other impurities makes the gypsum unsuitable for construction or other purposes.

Since sulfate reducing bacteria (SRB) are known to be able to use the sulfate moity in gypsum in their normal metabolic activity (Ehrlich, 1990), our hypothesis was that SRB, and possibly other bacteria, could use some component of the gypsum directly (e.g., sulfate in dissimilatory reduction), or otherwise breakdown gypsum and by so doing release (solubilize) Po in the process. To test this theory we constructed plastic columns that were filled with sterile phosphogypsum (henceforth referred to as gypsum), and by varying the microbial consortia added to these columns and the attendant redox conditions, we were able to demonstrate a direct bacterial involvement in Po solubilization.

MATERIALS AND METHODS

Experimental Rationale

Gypsum is a very delicate material whose physical treatment can produce drastic and highly variable experimental results. When freshly collected, gypsum contains a substantial microbial population (about 10^7 cells/g) which were found to die off upon storage of the material over a six to eight month period. In our early experiments, variations in the microbial assemblage, particularly the SRB, led to erratic results. We had no way of maintaining consistency in the microflora over the time frame required between experiments. We also experienced considerable difficulty in arriving at suitable sterile experimental controls. All efforts at drying or autoclaving gypsum served only to decompose or otherwise alter the material itself, which again led to unpredictable results. Ultimately, ^{60}Co irradiation (a 1.8 megarad dose administered over a 24 hr. period) yielded a sterile and stable product suitable for our purposes.

Since variation in the natural gypsum microflora would unpredictably affect experimental outcome, we decided to isolate a number of bacterial cultures from freshly collected gypsum samples and to then add these cultures back to sterilized gypsum to insure consistency of the bacterial consortia and inoculum size between experiments. In this manner, we were also able to illustrate the role of SRB by comparing systems to which they had been added to ones in which they were omitted.

Although the radionuclide levels are of environmental concern, the amount of ^{210}Po in gypsum is such (40-60 dpm/g) that it is necessary to use relatively large quantities, and to carry out the experiments over extended periods of time in order to measure releases at reasonably precise levels. The only practical approach that encompasses these requirements is the use of percolation columns that allows for the continual introduction of nutrients and the removal of Po-enriched spent medium.

Bacterial Culture Isolation and Maintenance

Phosphogypsum was collected in five gallon containers from an abandoned stack belonging to IMC Fertilizer Inc., Mulberry, FL. A culture medium (PYE) was used to both isolate the bacterial cultures and serve as a growth medium in the column experiments that contained peptone (0.08%), yeast extract (0.02%) and mineral salts (inorganic salts, g/l: Na_2SO_4, 0.02; NH_4Cl, 0.25; NaCl, 1.0; $MgCl_2.6H_2O$, 0.4; KCl, 0.5; $CaCl_2{\cdot}2H_2O$, 0.07 and KH_2PO_4, 0.10: trace metals, µg/l: $MnCl_2$, 0.1; $CoCl_2{\cdot}6H_2O$, 190; $ZnSO_4{\cdot}7H_2O$, 144; H_3BO_3, 6.0; $NiCl_2{\cdot}6H_2O$, 24.0; $CuCl_2{\cdot}2H_2O$, 2.0; $Na_2MoO_4{\cdot}2H_2O$, 36.0; $FeCl_3{\cdot}6H_2O$, 1600). When SRB were used in column experiments sulfate was eliminated from the medium so that the gypsum itself could serve as the sole sulfate source in the system. When a solid medium was needed for isolation and culture maintenance, agar was added for a final concentration of 1.5%.

A total of four bacterial cultures were isolated under aerobic conditions by shaking freshly-collected gypsum in a mineral salts diluent, surface streaking plates and incubating the samples at room temperature in the laboratory. A SRB culture was isolated by filling screw cap tubes (16 x 150mm) with PYE medium, including sulfate, adding gypsum and allowing the mixed community to develop. Subcultures were taken from those tubes that had blackened (indicating FeS formation) and smelled of sulfide and transferred to sulfate API broth medium (Difco Laboratories, Detroit, MI) contained in screw cap tubes (16 x 150mm). As the SRB developed samples were taken and used to inoculate sulfate API plates that were then incubated anaerobically in a GasPak system (BBL, Cockeysville, MD). Single colonies were selected for repeated culturing until a pure culture was obtained.

For the column experiments all four of the aerobically-isolated cultures were grown on PYE plates, harvested and mixed together in equal proportions yielding a mixture henceforth referred to as BACT. Two mL of BACT suspension were added to each column and yielded a final cell density of approximately 10^7 bacteria per gram of gypsum, which was comparable in size to the naturally occurring bacterial community found in the gypsum stacks. The SRB, when needed, were grown in the PYE broth and 2 mL of the suspension added to each column.

Column Construction

The use of percolation columns enabled us to use a large mass of gypsum, between 100 and 300 g depending on the column size, which was an important consideration since the Po activity for the gypsum used was only 42 dpm/g. In those experiments in which we added cultures to sterile gypsum, 19mm ID polystyrene columns filled with 100g gypsum were used because of the limitation on their dimensions imposed by. the ^{60}Co irradiator used for sterilization. When unsterilized gypsum containing natural microflora were used in experiments (either in conjunction with or without BACT or SRB) 30-mm diameter polystyrene columns were filled with 300g of gypsum.

In all but two of the experiments described, the gypsum was first sterilized by irradiation (1.8 magarads) and the appropriate bacterial cultures were subsequently added. This approach was necessary since we found that the native microflora died as the gypsum aged which in turn introduced unexplained variation between experiments. Admittedly adding bacteria to sterile gypsum does not accurately depict natural processes, but it does afford a high degree of control in our experiments so that interactions between microbes and Po could clearly be demonstrated. In particular, this approach was the only way to delineate the role of SRB.

Aside from their dimensions, the large and small percolation columns were constructed in an identical fashion. The bottom was plugged with a rubber stopper that had a 1-cc plastic syringe barrel pushed through it that served as an outflow nozzle. The tip of the syringe was opened slightly to facilitate fluid flow, but under experimental conditions the syringe always held some of the exiting medium that served as a barrier to prevent air from entering. Above the rubber plug was placed 5 cm of Teflon lathe turnings (obtained from a machinist who worked with the material) that served to support the gypsum and promote the flow of spent medium out of the column. Next, gypsum was added to within 5 cm of the top of the column and a second stopper inserted that contained two short glass tubes through which medium, air or an inert gas (either hydrogen or nitrogen were used) could be introduced. The nutrient media was pumped through the column at a rate of 65 mL/day using a Harvard Apparatus peristaltic pump. Air and H_2-N_2 were first passed through cotton filters and then into the columns in order to prevent flooding and either prevent anoxia (air) or promote anoxia (H_2-N_2).

Polonium and Sulfide Analysis

The procedure for Po analysis was that of Harada *et al.* (1989). Column effluents were collected over one (65 mL), two (130 mL) or three (195 mL) day periods and one mL of concentrated HCl added to the sample containers, which were stored until assayed at the end of the experiment. Each analysis began by adding one mL of a ^{209}Po tracer (22.2 dpm/mL) to a known volume (depending on the duration of sample collection) of column effluent in 250 mL Teflon beakers.

The samples were digested by adding concentrated HCl (2 mL) and 60% perchloric acid (2 mL) and evaporating to dryness on hot plates. The residue was dissolved in 2.5 mL HCl, 1 g of hydroxylamine hydrochloride and 0.1 g of ascorbic acid were then added and the mixture diluted to 50 mL with distilled water. A 25-mm diameter silver disk (M10331, United Mineral and Chemical Co., Lyndhurst, NJ) that had been covered on the back side with plastic electrical tape, was placed in the digest solution and the ^{209}Po and ^{210}Po allowed to self-plate onto the front of the disk for three hours at a temperature of 85 - 90°C. After plating the disk was rinsed with distilled water and counted in an a-spectrometer.

Sulfide analysis was performed according to the method of Cline (1969) on 2mL aliquots of column effluent as needed.

RESULTS

The first experiment performed was to determine if bacteria had any effect on PO release from gypsum. Columns were set up that had the following treatments: (1) freshly-collected gypsum; (2) sterilized gypsum to which BACT and SRB were added; (3) unsterilized gypsum to which BACT and SRB were added; and (4) a sterilized, uninnoculated control. Results are reported either as the cumulative PO released **(Figure 4-1),** since this is how gypsum newly added to a storage stack would behave, and as a daily release rate **(Figure 4-2)** which illustrates the temporal sequence of release after bacteria were added, or other treatments begun.

Medium was first pumped through the columns for seven days, after which bacteria were added to two of the columns and PO release monitored for a total 25 days. Before examining the bacterial effects, it is important to note that the sterilized control shows some Po release which is most pronounced in the first day of the experiment (Fig. 4-2). We assume that this apparent release is associated with fine particles that passed the teflon turnings at the bottom of the column.

The general conclusions from this experiment are that bacteria do affect a significant enhancement in PO release, whether the column is simply flushed with medium and the natural microflora allowed to proliferate (Fig. 4-1, solid squares) or whether amended with laboratory grown cultures (Fig. 4-1, open squares). The addition of bacteria to the sterilized gypsum at day 7 yielded a dramatic enhancement of PO release (Fig. 4-1, open diamonds), as did the addition of bacteria to untreated gypsum (Fig. 4-1, open squares). The effects of SRB became evident by day 10 when the two columns to which they had been added turned black.

The daily Po release showed a dramatic increase resulting from the addition of bacteria at day seven, but then decreased at the time when the column turned black because of the presence of FeS. Since Po also reacts with sulfide to form PoS_2 (Bagnall, 1966), or could presumably co-precipitate with FeS, the presence of elevated

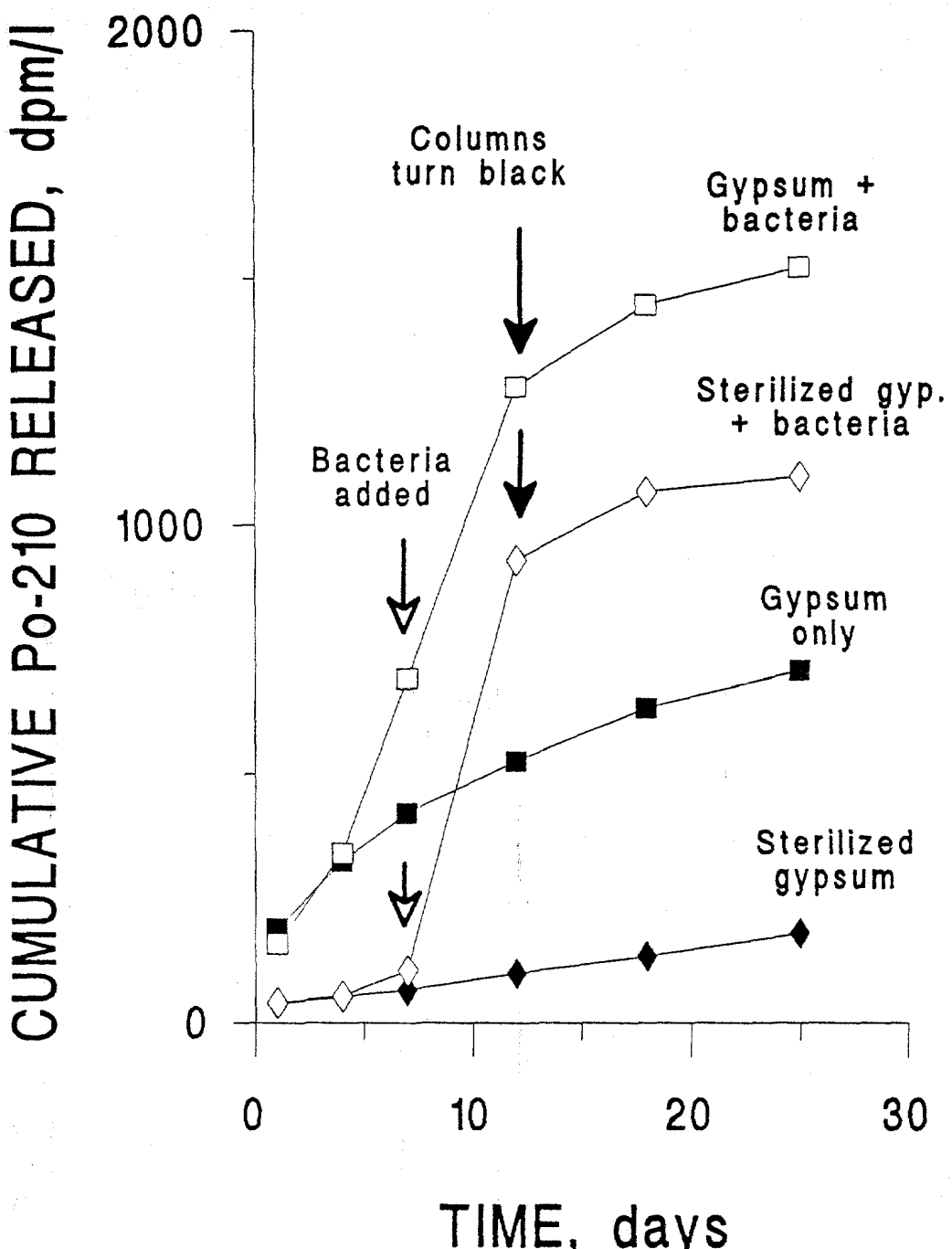

Fig. 4.1. The effect of naturally occurring and cultured bacteria on the cumulative release of Po from gypsum. Columns received the following treatments: the natural gypsum microflora alone (solid squares), the natural gypsum microflora plus the BACT-SRB mixture (open squares), sterilized gypsum plus the BACT-SRB mixture (open diamonds) and sterilized gypsum alone (solid diamonds). The arrows indicate when BACT-SRB were added or when the columns turned black indicating FeS formation.

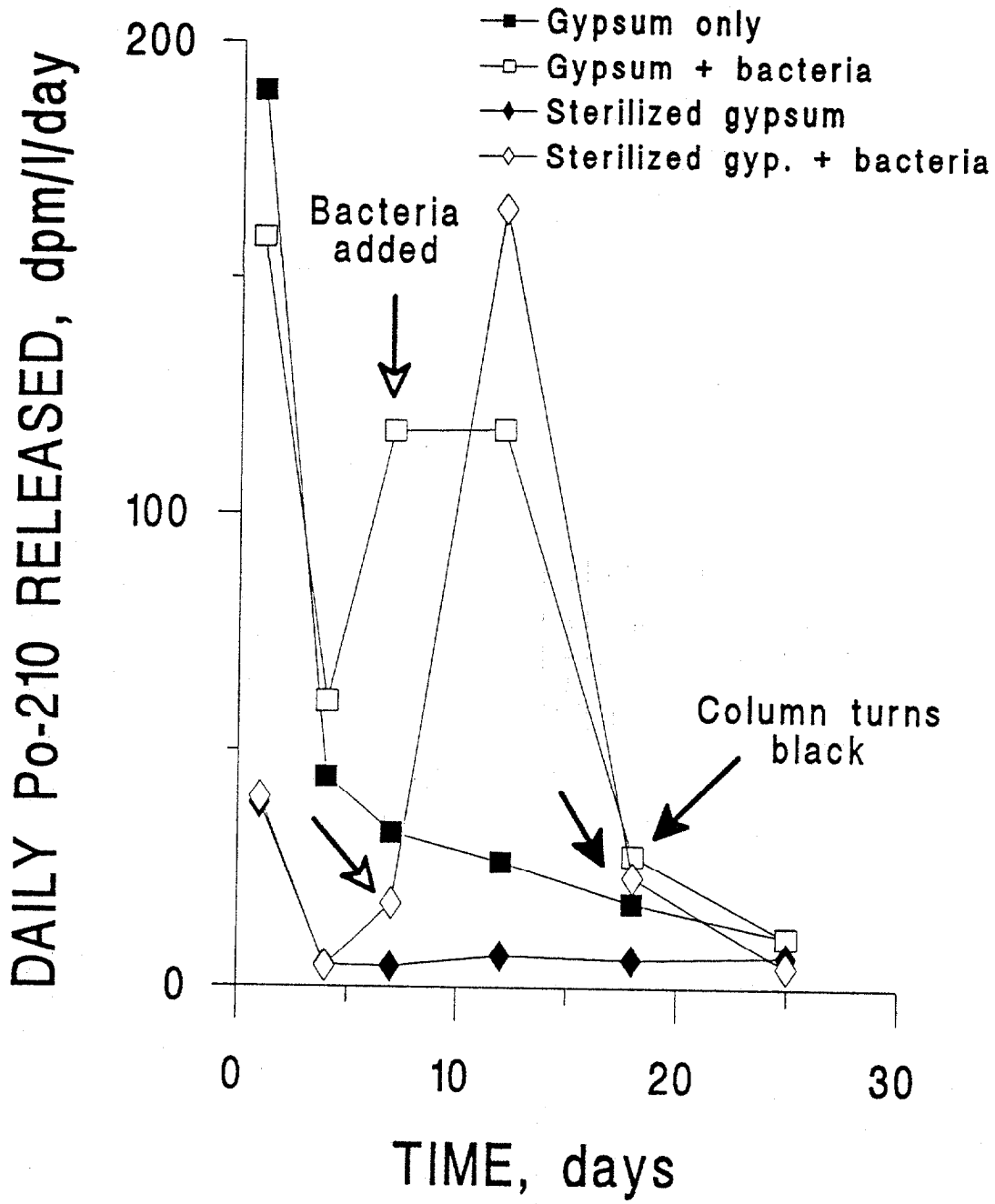

Fig. 4.2. The daily release rate of Po from gypsum columns. Symbols and treatments are the same as in Fig. 1.

sulfide might actually serve to prevent Po mobilization and migration from gypsum. Thus, the effects of SRB on Po solubilization is mixed. SRB apparently can use the sulfate moity in gypsum and mobilize Po in the process. Although destroying the gypsum would facilitate Po release, the sulfide produced by SRB metabolism could serve to precipitate Po under appropriate conditions.

In an effort to further elucidate the role of SRB, a series of columns were prepared in which the BACT mixture was added to sterilized gypsum, either alone or together with SRB. Duplicate columns of each microbial mix (two columns each of BACT and two of BACT plus SRB) were prepared and air pumped through one of each paired column in an effort to prevent fluids from accumulating and at the same time raise the redox level. The anticipated effect was to retard SRB and foster auto-oxidation in the air-purged columns relative to their unpurged companions. Initially, both columns with SRB showed the most rapid PO release until day 10 when the column without air turned black indicating the formation of FeS **(Figure 4-3**, open diamonds). The companion column (purged with air) did not blacken and continued to release Po for the remainder of the experiment (Fig. 4-3, solid diamonds).

The columns that contained the BACT mixture alone (no SRB) also mediated enhanced Po release (Fig. 4-3, open and solid squares). Again the air-purged column afforded more extensive Po solubilization than did the unventilated column.

The daily Po release rate for the SRB columns was essentially identical for the first 10 days, but after FeS appeared (and presumably PoS) the unventilated column had a dramatic reduction in Po release to a rate of approximately 1 dpm L^{-1} Day^{-1}, equivalent to the sterilized control (**Figures 4-4** and **4-5**). In contrast, the air-purged column continued to release Po at a significant level. The daily release rates for the BACT mixtures and the control indicate decreasing activity in the order BACT plus air, BACT and control. Exponential regression curves of the type $y = Be^{-mt}$ were fit to the daily release data to provide further quantification of these observations. In this instance B would represent the initial release, -m would be equivalent to a release rate constant, and t is elapsed time. Of primary concern is the rate constant -m, since it determines just how long and to what extent Po will be mobilized under the specific experimental conditions. From the data in **Table 4-1** it is apparent that the passage of air through the columns facilitated Poirelease to an equivalent degree whether SRB were present or not (-m = 0.026). In contrast, the presence of SRB under more anoxic conditions appears to bind Po (-m = 0.060) thus affording even less mobilization than observed with sterile gypsum alone (-m = 0.050). These results indicate that bacteria, including SRB, do in fact mediate Po dissolution from gypsum, but the process is affected by redox conditions and sulfide levels.

In the previous experiment it was evident that SRB potentially play a major role in Po mobilization, depending on the level of sulfide produced in the course of their metabolic function. In an effort to quantify the effects of SRB still further, we

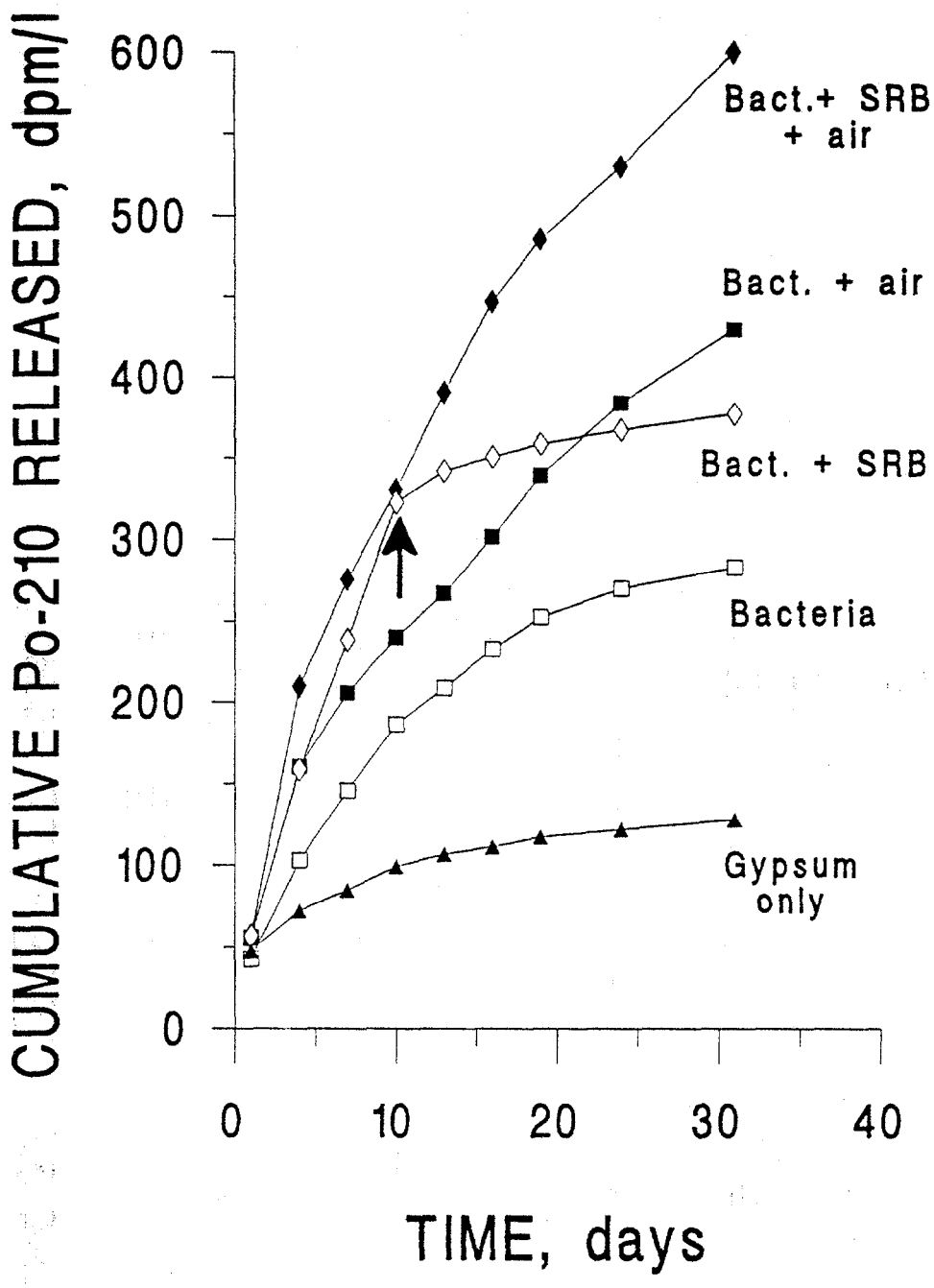

Fig. 4.3. The effect of purging the columns with air to control redox conditions. Sterilized gypsum columns were treated as follows: BACT addition (open squares), Bact+SRB addition (open diamonds), BACT plus air purging (solid squares), BACT+SRB plus air purging (solid diamonds), gypsum alone (solid triangles). The arrow indicates when the unpurged BACT+SRB column turned black indicating the formation of FeS.

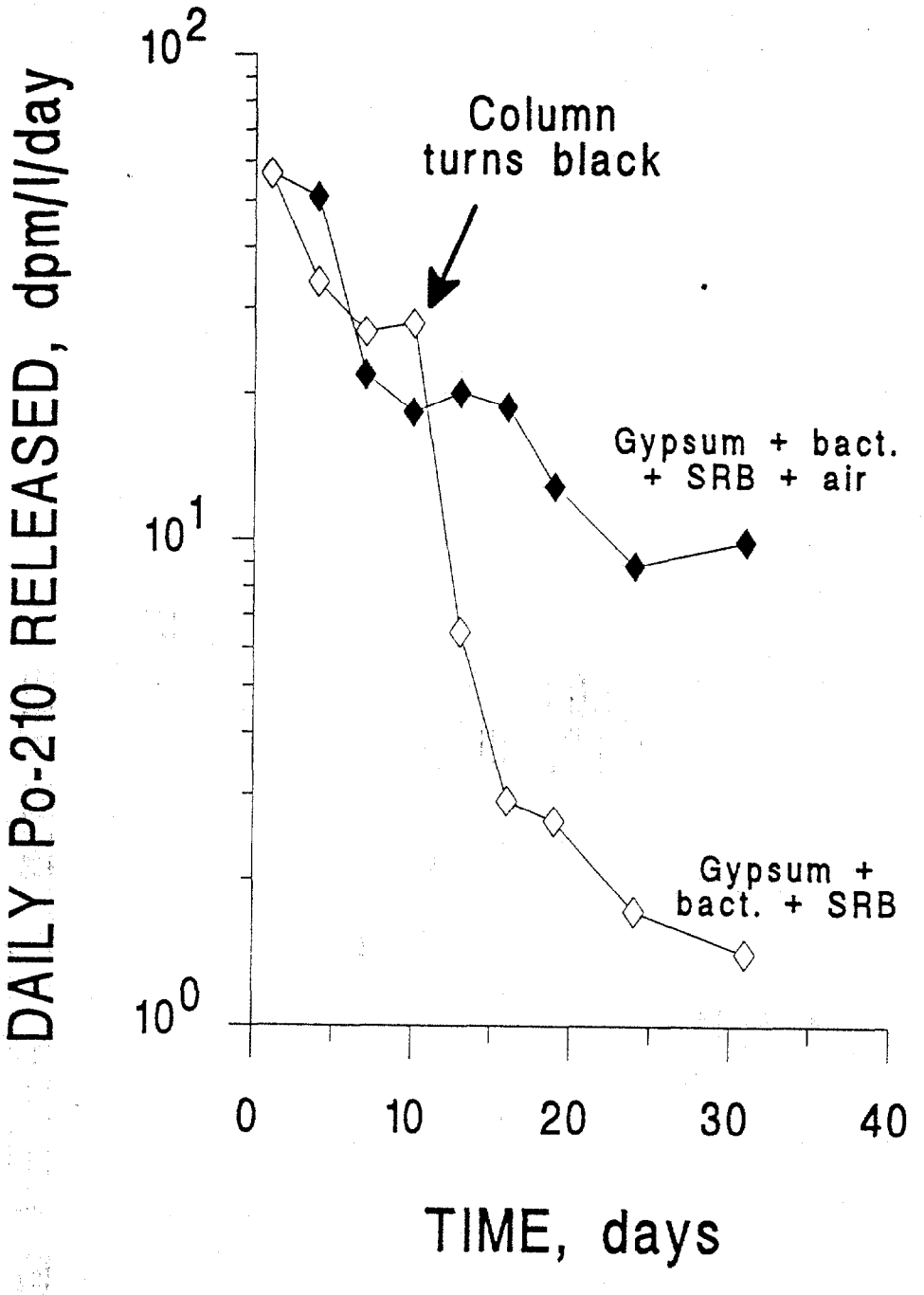

Fig. 4.4. A comparison of the air purged and unpurged columns containing SRB. Once FeS forms in the unventilated column Po release ceases dramatically. Symbols: Solid diamonds, BACT+SRB plus air; open diamonds, BACT+SRB only.

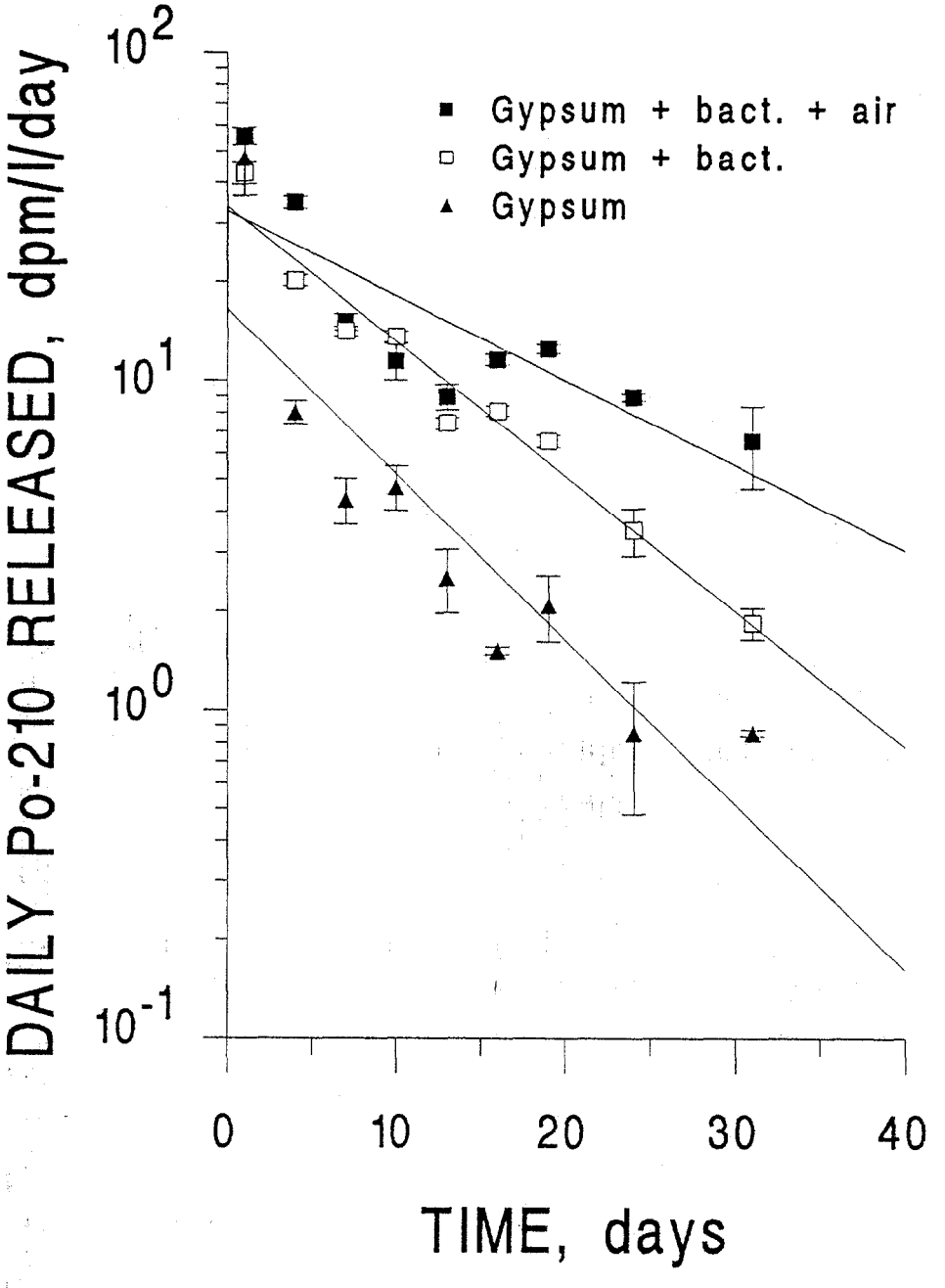

Fig. 4.5. Polonium release by the BACT mixture alone with and without air purging. The treatments were: BACT plus air (solid squares), BACT without air (open squares), and gypsum alone (solid triangles).

Table 4.1. Removal rate constants for polonium[a].

Column Manipulation	Removal Rate Constant (-m)
BACT + SRB + Air	- 0.026
BACT + SRB	- 0.060
BACT + Air	- 0.026
BACT	- 0.041
Control	- 0.050

[a] An equation of the type, $y = B \times e^{-mt}$ was fit to the daily release data. In this equation, y indicates Po released (dpm day^{-1}), B is the initial release, -m is the removal rate constant, and t is the elapsed time (days).

performed a experiment in which SRB activity would either be promoted or hampered and the effects of SRB activity determined by changes in Po and sulfide released from the columns. In a closed or strongly reducing environment, SRB should rapidly develop and sulfide levels would be expected to reach elevated concentrations, whereas the introduction of air would at least serve to reduce the sulfide level, as well as raise the overall redox conditions within the gypsum by preventing flooding. Under such a regime we would expect to see very little PO released in the strongly reducing environment with active SRB, if Po is scavenged by insoluble sulfides. Furthermore, measuring sulfide and Po contained in the column effluent would provide some index of how these elements interacted.

Columns of sterile gypsum were thus prepared with the following amendments: (1) the BACT consortium was added followed by air purging; (2) the BACT consortium plus SRB were added followed by air purging; (3) the BACT plus SRB were added followed by purging with either hydrogen or nitrogen; and (4) a column was run unamended to serve as a sterile control. The outcome of this experiment (Figure 4-6) clearly indicated that the complete bacterial mixture, including SRB, when purged with air affords the greatest polonium solubilization. The air-purged bacterial mixture (without SRB) had the second greatest polonium release followed by the sterile control and finally the anoxic column with SRB. Sulfide measurements of the column effluents (Table 4-2) revealed that the hydrogen/nitrogen purged column contained 30-fold more sulfide than the air-purged SRB column indicating that the SRB were active under both conditions. The elevated polonium release in the air-purged SRB column relative to the air-purged bacteria column (a 40% increase in polonium when SRB are present) further indicated that SRB do actually participate in polonium solubilization and that polonium is free to migrate through the column provided the sulfide concentration is maintained at very low levels ($\leq 10 \mu M$). If it is assumed that the same processes are taking place in the hydrogen/nitrogen column, then we can conclude that high sulfide concentrations serve to scavenge polonium and may in fact afford a mechanism to remove polonium from stack effluent or the groundwater. The daily release rates of polonium from the anoxic SRB column are even less than those of the sterile control once the sulfide levels have risen (Figure 4-7).

The experiments described to this point all involve the addition of cultures to sterilized gypsum in order to demonstrate the ability of bacteria to affect polonium solubilization. These experiments only establish the potential for such a process and do not address the extent to which it may occur in the environment. In order to arrive at an approximation for polonium dissolution by the native gypsum microflora, fresh gypsum samples were collected and immediately packed into a set of columns and transported back to the laboratory where the following experiments were begun within three days: (1) groundwater (pH 6.8), collected from the same site, was pumped through the gypsum; (2) the same nutrient solution as used our previous laboratory experiments was passed through the gypsum; and (3) this column was sterilized and fed autoclaved groundwater. The results (**Figures 4-8** and **4-9**) indicated that there was little difference between the sterile control and the

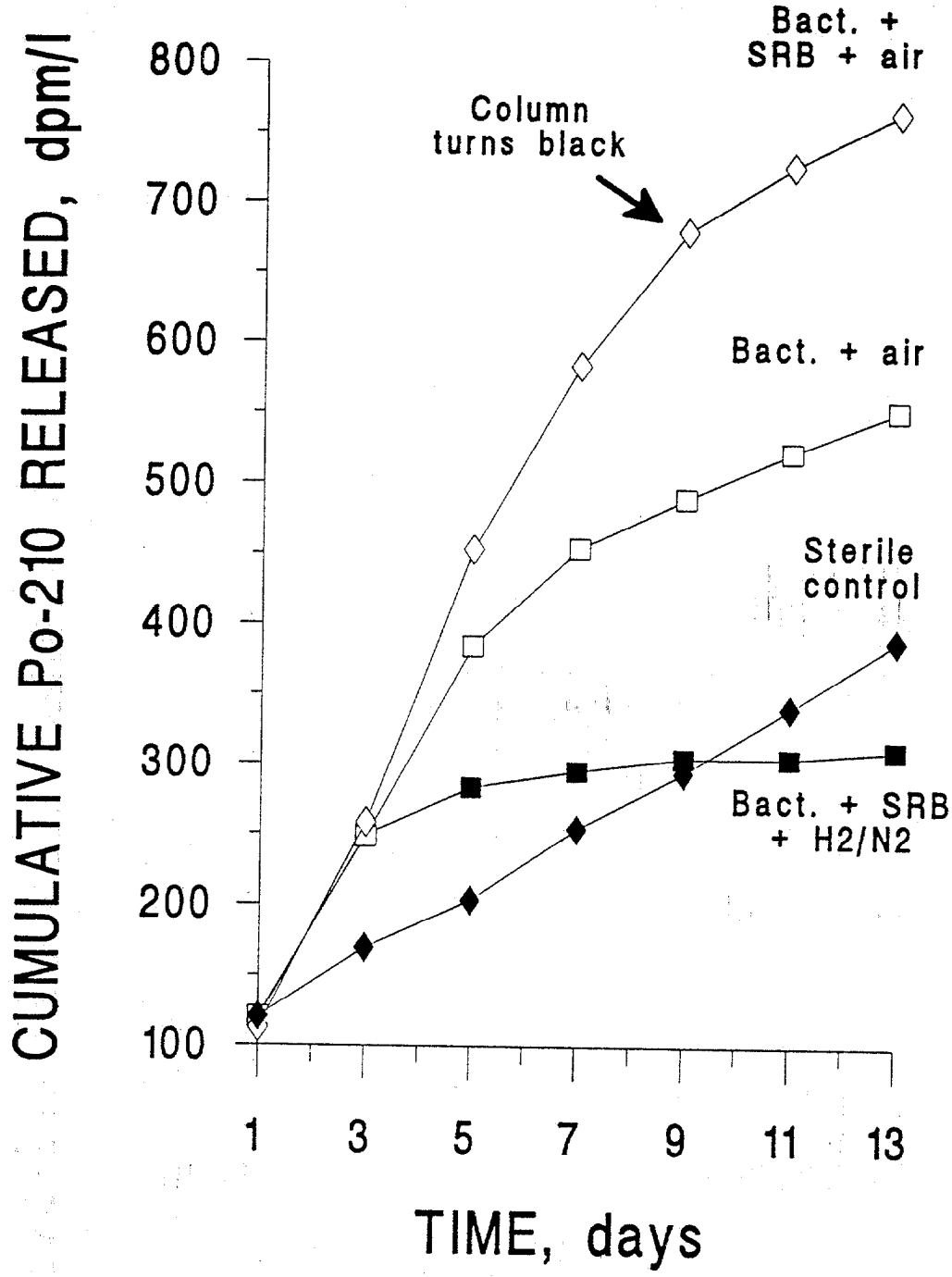

Fig. 4.6. The effect of initiating anaerobiosis by purging with either H_2 or N_2 gas. Air purging enhanced Po release while inducing anaerobiosis and SRB activity reduced Po release. The treatments were: BACT+SRB plus H_2-N_2 (solid squares), BACT+SRB plus air (open diamonds), BACT plus air (open squares), gypsum alone (solid diamonds).

Table 4.2. Sulfide concentration (μM) in each column.

Elapsed Days	Bact. + SRB & H_2/N_2 gas	Bacteria & aeration	Bact. + SRB & aeration	Control
5	260.58	3.15	7.95	BDL
7	215.32	BDL[a]	8.94	BDL
9	226.64	0.32	5.38	BDL
11	198.35	BDL	BDL	BDL
13	215.32	BDL	BDL	BDL

[a]BDL indicates below detection level.

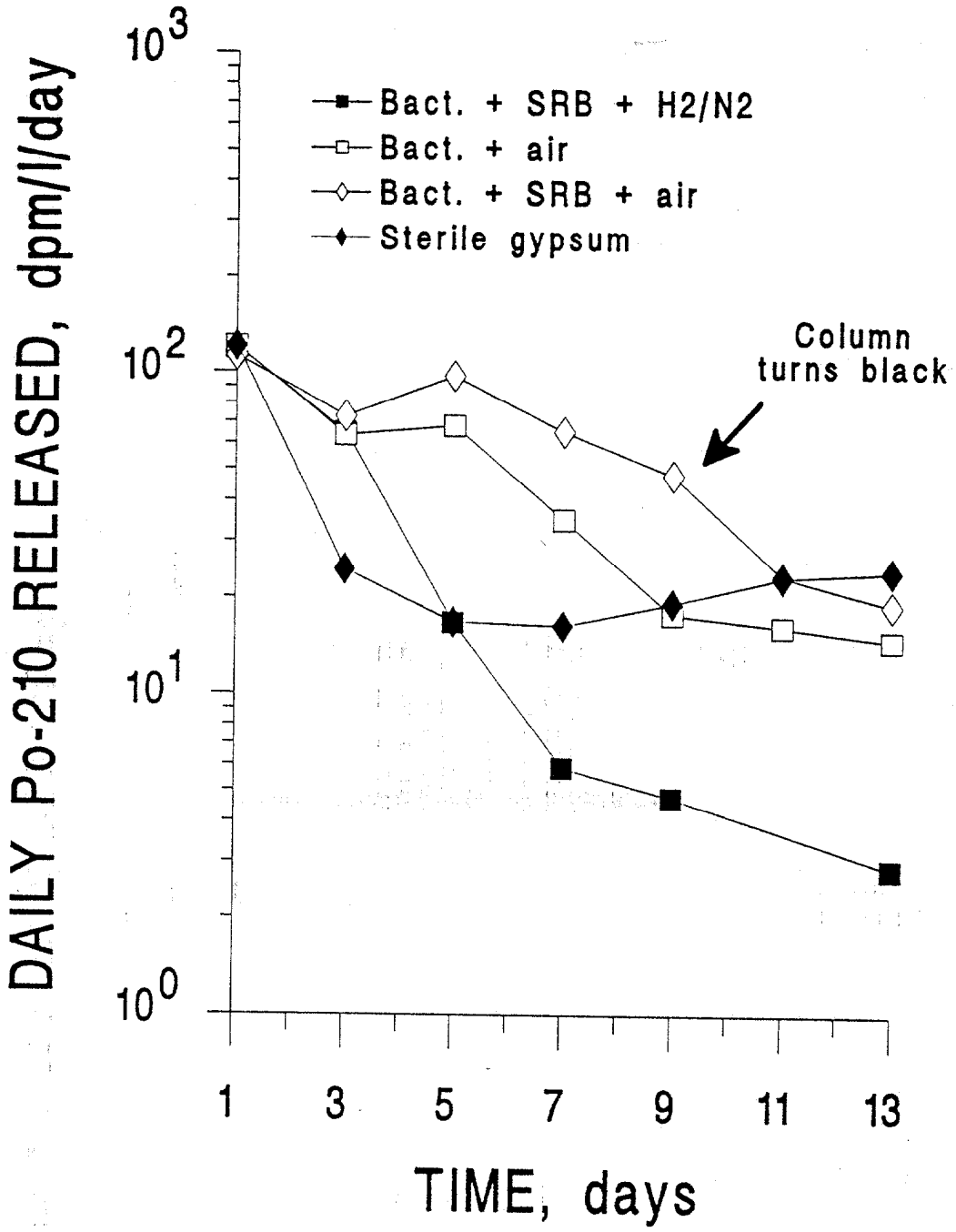

Fig. 4.7. The daily Po release under air and N_2-H_2 purging. Symbols and treatments are the same as in Fig. 6.

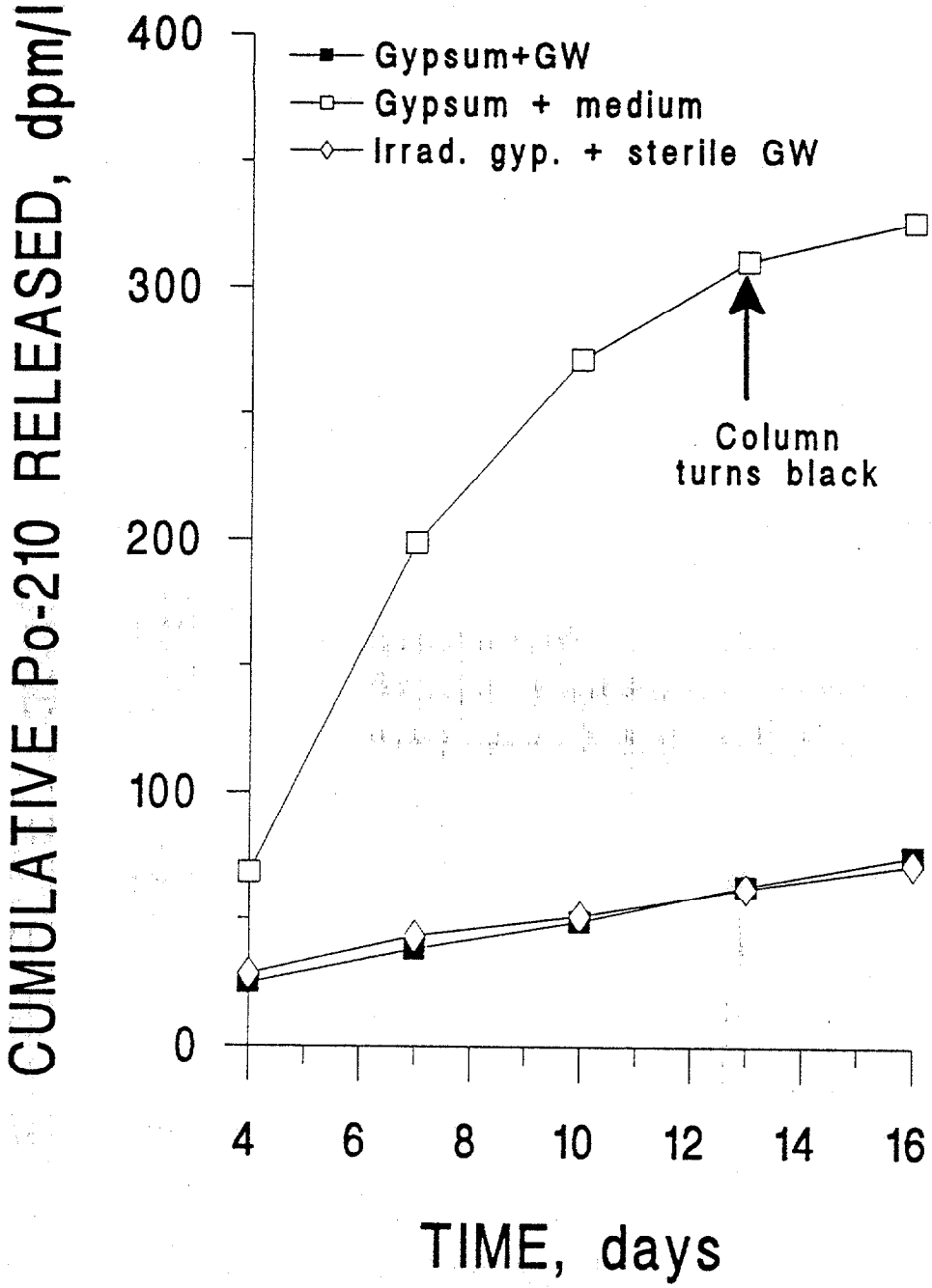

Fig. 4.8. Polonium release by naturally occurring gypsum microflora under varying nutrient conditions. Symbols: gypsum fed ground water (solid squares), sterile gypsum fed sterile ground water (open diamonds), gypsum fed PYE medium (open squares).

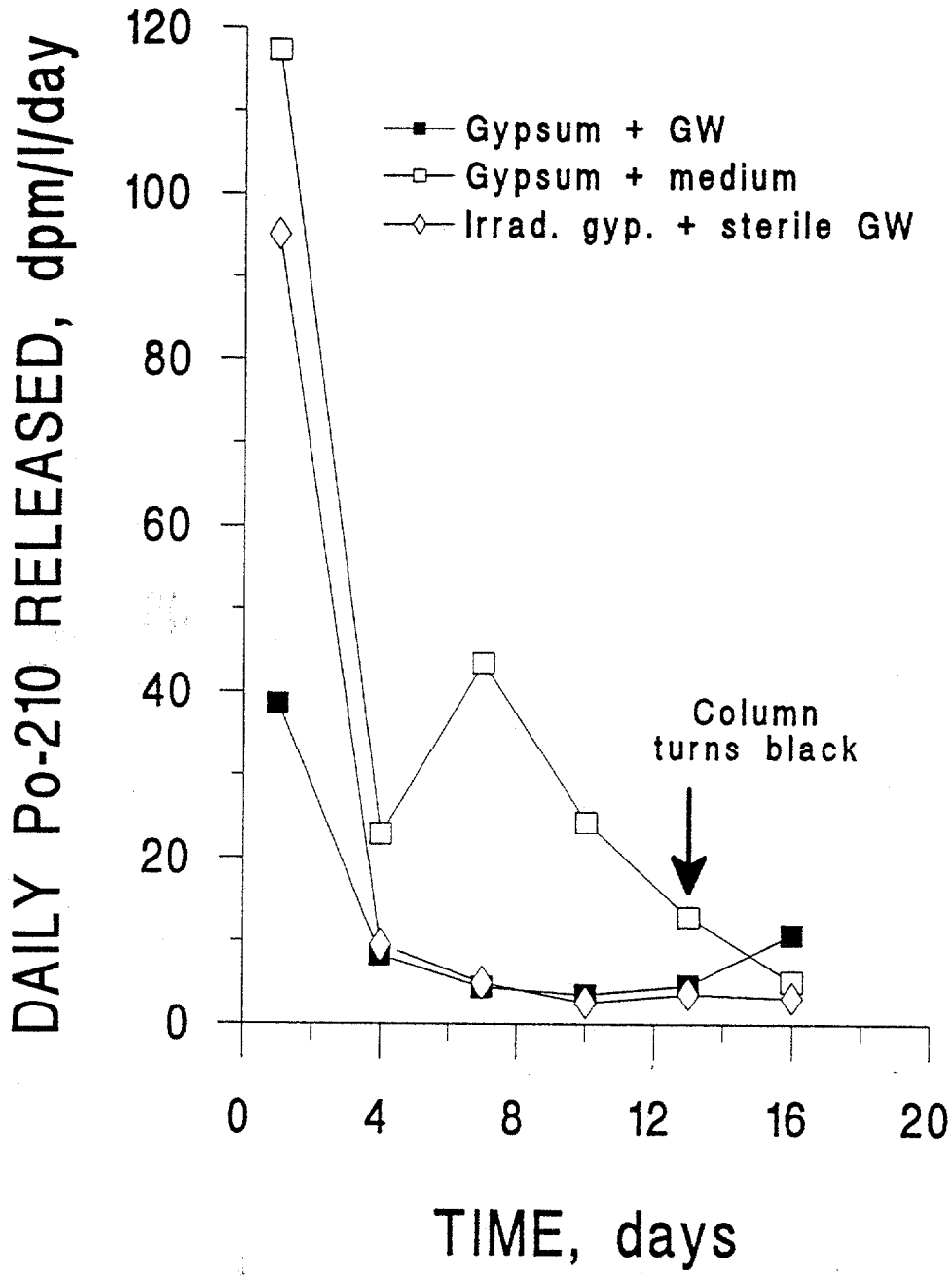

Fig. 4.9. Daily Po release by naturally occurring gypsum microflora under varying nutrient conditions. Symbols and treatments are the same as in Fig. 8.

untreated gypsum when the columns were pumped with groundwater, although the daily release rate for the freshly-collected gypsum did increase by day 16. However, when the gypsum was fed a nutrient-rich solution there was a significant increase in polonium release that had been mediated by the natural microflora. These findings confirm the results from our previous experiments, namely, that bacteria do mediate Po release when their growth is fostered and further suggest that polonium dissolution may be a fairly widespread property among the regional microflora provided there is an adequate nutrient source. We have no way of knowing the nutritive value of the process waters and other solutions that pass through the gypsum stacks but this experiment suggests that by making substrate resources available, the natural microflora will mediate significant polonium releases.

Several years prior to the current research effort we measured bacterial community growth rates in groundwater collected from a shallow monitor well known to have elevated (>1000 dpm) ^{210}Po activities (Harada *et al.*, 1989). Growth rates were determined by a pulse labeling technique (LaRock, *et al.*, 1988) over a one year period between 1988 and 1989 in order to assess growth potentials. The reciprocal of community doubling time (multiplied by 100 to provide a index of growth) was compared to temporal changes in ^{210}Po concentrations and the average annual rainfall for the area (**Figure 4-10**). During the period between Sept. 1988 and March 1989 there was a decline in the groundwater community growth to the point where the growth rates become zero or negative indicating that the population was unable to sustain itself and was in a state of decline. This same period coincided with a annual minimum in rainfall and a simultaneous reduction in groundwater Po concentrations. As rainfall increased in March 1989, the groundwater bacteria become active again and there was a concomitant increase in Po levels. We cannot state unequivocally that bacteria were the sole cause for the observed changes in ground water Po, but in light of the findings in this paper, bacteria will in some measure alter Po levels provided their growth is facilitated.

DISCUSSION

We conclude from these experiments that: (1) bacteria are capable of releasing polonium from the gypsum matrix in which it is bound; (2) SRB enhance polonium release provided the sulfide levels resulting from their metabolism do not become excessive, i.e., remain below approximately 10 μM; and (3) naturally-occurring microflora will serve to mobilize polonium depending upon the nutrient resources made available to them.

The finding of Po as the sole a-emitting nuclide, accompanied by low sulfide concentrations, in some ground water systems can best be explained by bacterial action such that Po is selectively mobilized over its radiogenic parent and enabled to migrate through the aquifer system. Since sulfide accompanies Po one logical release mechanism is a direct reductive attack on the sulfate moity of gypsum that

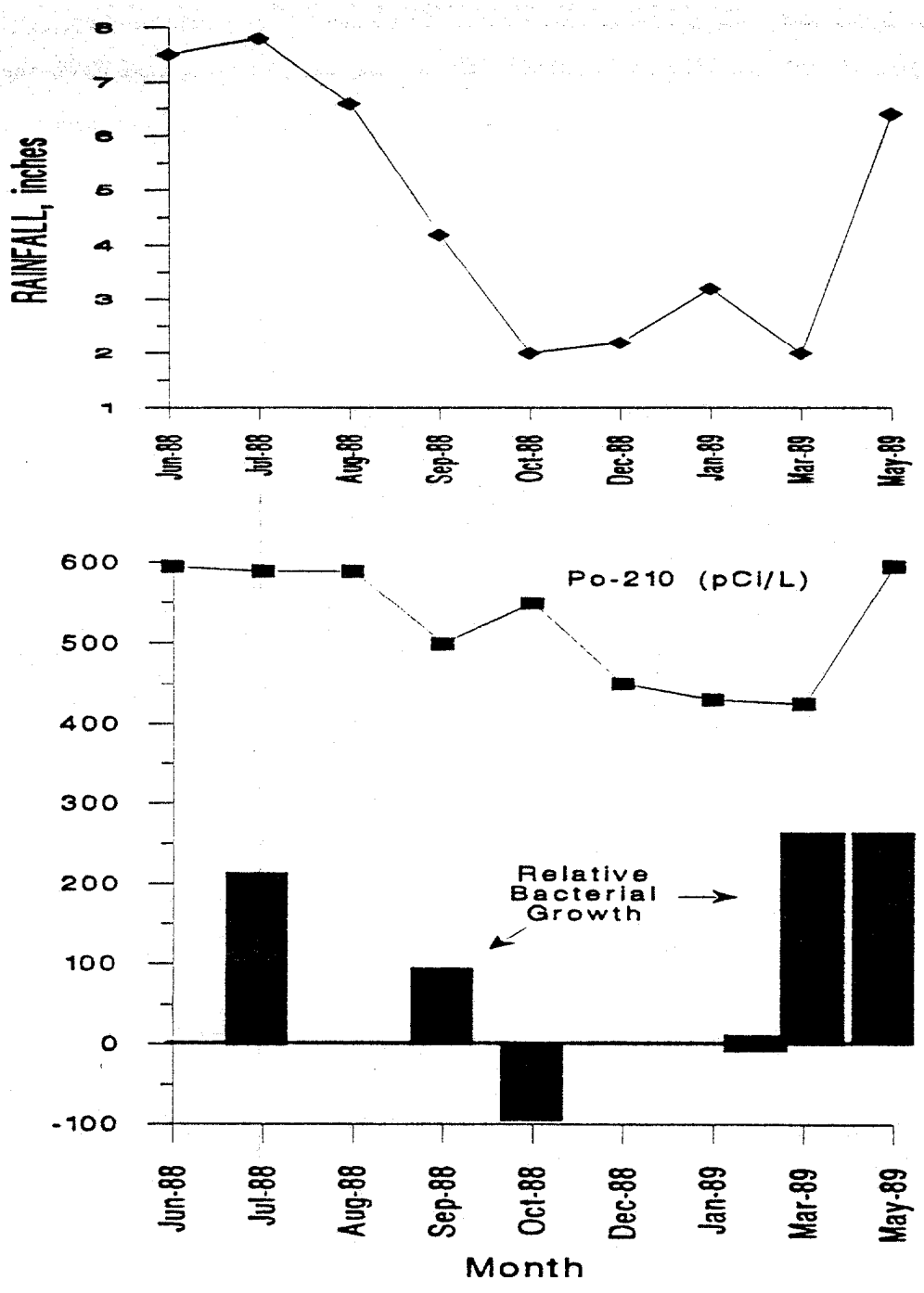

Fig. 4.10. Seasonal variations in rainfall, ground water Po concentrations and ground water bacterial growth rates.

ultimately frees Po by some undefined process. Zajic (1969) reported that microbial sulfate reduction was responsible for gypsum decomposition that resulted in the release of dissolved Ca. Bolze *et al.* (1974) and McCready and Krouse (1980) demonstrated that SRB were capable of utilizing barite, and Fedorak *et al.* (1986) reported on the release of Ba and ^{226}Ra from a Ba-Ra sulfate sludge accompanied by the production of sulfide. The ability of bacteria to incorporate Po into cellular protein has also been demonstrated (J. Cherrier, Master's thesis, Florida State University, 1992; Cherrier, Burnett and LaRock, 1994) indicating at least a potential for assimilative Po reduction and a biochemical role analogous to that of sulfur. It is not unreasonable in light of the findings we present here, to suggest further that Po undergoes a dissimilatory reduction that facilitates its solubilization and migration through ground water in a manner similar to sulfate reduction.

An important controlling factor appears to be the availability of nutrients to the bacterial community. When we added organic substrates to the native assemblage (Fig. 4-8) Po release began immediately. Similarly, field measurements revealed a direct relationship between bacterial growth and Po levels that coincided with the annual rainfall pattern (Fig. 4-10). Since water is the primary vehicle for transporting nutrients through soils it is not unreasonable that rainfall should exert a controlling influence on microbially mediated Po release.

In all of our experiments we noted a decline in the daily Po release rate as the experiments progressed. The gypsum used had been stored in the stockpile for over a decade before we collected material for use in these experiments, and was very dense and compact. In preparing our columns, the gypsum was loosely added to the cylinders, but became compacted as medium flowed through this material. The volume was observed to decrease by as much as 15% and consequently would have the effect of decreasing porosity and thus limiting oxygen and nutrient availability both of which serve to reduce Po solubilization to some lower, but steady level depending on physical and nutritional conditions.

In our experiments with SRB we found an enhancement of Po release only in those cases where we were able to maintain sulfide levels of 8 µM or so (Fig. 4-6 and Table 4-2). The work of Harada *et al.* and of Burnett *et al.* (1987) also reported high Po concentrations (on the order of 1,000 dpm/l) in the presence of sulfide levels that were on the order of 10 µM or less. These findings suggest that at the low levels encountered (<10 µM) Po and S can coexist and do not precipitate. At higher sulfide levels, it is likely that some other metal sulfide becomes important and co-precipitates Po.

While it is easy to envision a direct link between the metabolic activity of the SRB and Po utilization, different mechanisms must also be applicable if aerobic, nonspecific bacteria are capable of releasing Po. One of the more interesting aspects of Po chemistry is that Po reacts to form complex ions in acid media. Oxalic and phosphoric acids are both known to form complexes with Po, and as such raises the possibility of interactions with end products that are produced as a result of bacterial

catabolism. Carbonic or organic acids are produced by bacteria as are naturally occurring complexing agents such as carboxylic acids (Ehrlich, 1990; Silverman and Ehrlich, 1964). Our present effort offers no definitive explanation on how the BACT mix affects Po solubility, but indicates only that there are mechanisms other than direct enzymatic attack that may be operative in these systems.

Our findings also suggest that manipulation of the gypsum microflora could be used as a remediation device to prevent selective Po solubilization. Since rainwater appears to be a principal environmental variable, it may be possible to prevent it from percolating through the gypsum stacks by installing impervious layers in the stacks as they are constructed. In experiments using newsprint that had been added to gypsum we found the mixture to be almost completely impervious to liquid flow. By adding used newsprint to gypsum, at say 10 to 20 foot depth intervals, it would be possible to economically isolate the deeper layers in storage stacks, and in so doing prevent (or retard) the microflora to such an extent that Po is no longer released.

A second mechanism which might be applied to control Po migration in gypsum stacks would be to enhance the activity of SRB. Recall in our experiments that those columns which were anoxic and had high sulfide levels, did not release any significant Po to the column effluent (Figs. 4-3 and 4-6). Interestingly, when newsprint was added to fresh gypsum, a very active SRB population quickly developed causing the mixture to blacken with FeS. Such SRB activity would not prevent Po from being released by microbes acting directly on the gypsum, but the associated sulfide would act to effectively scavenge the Po in place.

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APPENDIX A

Detailed Sample Descriptions

APPENDIX A Phosphogypsum, phosphate rock, and miscellaneous samples collected from fertilizer companies in Florida. Samples of Gyp-10, Gyp 53 - 60, Ore-10/1, Ore-10/2, Ore-53 and 54, and P-53 and P-54 were collected from the Occidental chemical plants in Northern Florida. All other samples of phosphogypsum, phosphate rock, and miscellaneous samples were collected from the Central Florida Phosphate District.

Lab Number	Company	Sample Notes	Date Collected or Received
		Phosphogypsum Samples	
Gyp-1	Estech	Stack inactive for 10 to 20 years, sample provided by FIPR.	1/02/90
Gyp-2	U.S. Agrichemicals Mulberry	Stack inactive for about 10 years, sample provided by FIPR.	11/02/90
Gyp-3	IMC New Wales	Sample collected ~ half way up stack in March 1990 and provided by FIPR.	11/02/90
Gyp-4	Farmland	Sample collected by Farmland personnel.	01/10/91
Gyp-5/1	IMC (P-21)	Collected from grey gypsum horizon ~2 m below summit on the west flank of the stack.	01/10/91
Gyp-5/2	IMC (P-21)	Collected in the weathered white gypsum horizon near the stack summit ~1 m above sample 5/1.	01/10/91

APPENDIX A (continued)

Lab Number	Company	Sample Notes	Date Collected or Received
Gyp-6	Royster	Collected from south stack; < 2 years old.	02/14/91
Gyp-7	Royster	Fresh phosphogypsum collected as a slurry.	02/14/91
Gyp-8	Royster	Collected from the east flank of the north stack; deposited decades ago.	02/14/91
Gyp-9	CF Industries (Bartow)	Collected from inactive stack. Deposited ~ 1989.	03/26/91
Gyp-10	Occidental	Approximately weeks to months old.	04/30/91
Gyp-11	Cargil Fertilizer	Collected from active portion of the stack.	06/04/91
Gyp-12	Farmland	South flank, ~ 10 m above base of stack.	11/07/91
Gyp-13	Farmland	South flank, ~ half way up stack.	11/07/91
Gyp-14	Farmland	Fresh gypsum, directly out of discharge line.	11/07/91
Gyp-15	Farmland	Collected near discharge line at summit of the stack; ~ 1 week old.	11/07/91

APPENDIX A (continued)

Lab Number	Company	Sample Notes	Date Collected or Received
Gyp-16	Farmland	NE corner, ~10 m above base of the stack.	11/07/92
Gyp-17	Farmland	North flank ~5 m above base of the stack. Believed to be the oldest portion of stack.	11/07/91
Gyp-18	Farmland	Fresh gypsum collected directly from the discharge pipe at the stack summit.	02/03/92
Gyp-19	Royster	Fresh gypsum collected directly from the discharge pipe at the stack summit.	02/03/92
Gyp-20	IMC (P-21)	Collected from near vertical surface ~3 m from the top of the old stack.	02/03/92
Gyp-21	CF Industries (Plant City)	Fresh gypsum collected directly from the discharge pipe at the stack summit.	02/04/92
Gyp-22	CF Industries (Plant City)	Collected next to pool at discharge lines at the stack summit; <1 week old.	02/04/92
Gyp-23	CF Industries (Plant City)	North side of stack summit; ~1 week old.	02/04/92

APPENDIX A (continued)

Lab Number	Company	Sample Notes	Date Collected or Received
Gyp-24	CF Industries (Plant City)	North flank of stack; ~2-3 years old.	02/04/92
Gyp-25	CF Industries (Plant City)	Collected behind mobile structure on stack; ~20 years old.	02/04/92
Gyp-26	IMC New Wales	Fresh gypsum collected from the "east train" of the reaction line.	03/27/92
Gyp-27	IMC New Wales	Sample deposited at the base of the SW flank of the stack ~1975.	03/27/92
Gyp-28	IMC New Wales	Sample collected ~25-30 m above the base on the south flank of the stack. Deposited in ~1980.	03/27/92
Gyp-29	IMC New Wales	Sample collected ~40-45 m above the base on the south flank of the stack. Deposited in ~1989.	03/27/92
Gyp-30	IMC New Wales	Sample collected in discharge channel at the stack summit; < 1 week old.	03/27/92

APPENDIX A (continued)

Lab Number	Company	Sample Notes	Date Collected or Received
Gyp-31	CF Industries (Plant City)	Fresh gypsum collected from discharge line onto the stack summit on 3/27/92. Sample provided by CF personnel.	03/27/92
Gyp-32	Seminole	Collected from the southwest corner of the north stack ~12 m from the base of the stack. Sample is ~ 23-35 years old.	06/17/92
Gyp-33	Seminole	Sample collected from the south side of the summit of the north stack. Sample was discharge within 1 to 2 weeks of the date of collection.	06/17/92
Gyp-34	Seminole	Fresh gypsum collected directly from the discharge pipe at the summit of the north stack.	06/17/92
Gyp-35	Seminole	Fresh gypsum collected from directly below the discharge pipe on the southwest corner of the summit of the north stack. Sample collected within minutes of discharge.	06/17/92

APPENDIX A (continued)

Lab Number	Company	Sample Notes	Date Collected or Received
Gyp-36	Seminole	Collected from the south stack on the northwest corner where the discharge lines were located. Phosphogypsum is ~3 weeks old. Stack temporarily inactive when sampled.	06/17/92
Gyp-37	Seminole	Sample collected from the southwestern corner of the south stack. Phosphogypsum deposited ~5-6 years prior to collection.	06/17/92
Gyp-38	Agrico, South Pierce Plant	Fresh gypsum collected directly from the discharge pipe at the summit of the stack. Sample provided by Agrico personnel.	06/22/92
Gyp-39	Agrico, South Pierce Plant	Sample collected from southwestern corner corner of the stack at the summit. Discharge lines have been at this location for ~2 years. Sample was ~1-2 days old	06/17/92
Gyp-40	Agrico, South Pierce Plant	Sample collected from southwestern corner corner of the stack ~20 m below the summit. Sample was ~3-4 months old.	06/17/92

APPENDIX A (continued)

Lab Number	Company	Sample Notes	Date Collected or Received
Gyp-41	Agrico, South Pierce Plant	Sample collected from the western retaining wall of cooling pond #6 ~2 m above the road. Sample was >6 years old.	06/17/92
Gyp-42	Agrico, South Pierce Plant	Sample collected from north side of stack on what is the oldest known surface 20-25 years).	06/17/92
Gyp-43	U.S. Agrichemicals Fort Meade	Sample collected from the western side of the stack ~4-5 m above the base in the road. Sample is 8-10 years old.	09/29/92
Gyp-44	U.S. Agrichemicals Fort Meade	Samples collected at the top of the stack on the NW corner in the discharge channel adjacent to the road. Two bags and a small bucket of phosphogypsum collect.	09/29/92
Gyp-45	U.S. Agrichemicals Fort Meade	Sample collected at the NE corner ~20 m above the base of the stack. Sample is about 3-4 years old.	09/29/92
Gyp-46	U.S. Agrichemicals Fort Meade	Sample collected at the NE corner ~14 m above the base of the stack. Sample is 5-6 years old. Large (5 gallon) bucket collected.	09/29/92

APPENDIX A (continued)

Lab Number	Company	Sample Notes	Date Collected or Received
Gyp-47	U.S. Agrichemicals Fort Meade	Fresh gypsum collected within the phosphoric acid plant subsequent to slurrying the gypsum, but prior to pumping the by-product onto the stack. OreS-47 was being reacted.	09/29/92
Gyp-48	IMC Nichols	Fresh gypsum collected directly from the discharge line on the stack. Dipper used for collection.	01/14/93
Gyp-49	IMC Nichols	Gypsum collected ~100 m directly SE of the discharge lines at the stack summit. Gypsum is 2 - 3 weeks old.	01/14/93
Gyp-50	IMC Nichols	Gypsum collected ~15-20 m below the summit on the western flank of the stack. Gypsum has been on the stack ~ 1 year.	01/14/93
Gyp-51	IMC Nichols	Gypsum collected on the western flank of the stack ~30 m below the summit and 8 m above the base. Gypsum has been on the stack ~6-8 years.	01/14/93

APPENDIX A (continued)

Lab Number	Company	Sample Notes	Date Collected or Received
Gyp-52	IMC Nichols	Gypsum collected in the dike wall of the cooling water pond on the SW corner of the stack. Sample collected ~2 m above the current water level. Gypsum has been on the stack >25 years.	01/14/93
Gyp-53	Occidental	Fresh gypsum slurry of DH from Suwannee River Complex. Sample of fresh DH was produced on this date. Sample provided by Occidental personnel.	01/15/93
Gyp-54	Occidental	Fresh gypsum produced in Swift Creek HH Comples on this date. Sample provided by Occidental personnel.	01/15/93
Gyp-55	Occidental	Sample collected from HH (Swift Creek) stack. Sample is 0 - 5 years old.	01/15/93
Gyp-56	Occidental	Sample collected from HH (Swift Creek) stack. Sample is 5 - 10 years old.	01/15/93
Gyp-57	Occidental	Sample collected from HH (Swift Creek) stack. Sample is 10+ years old.	01/15/93

APPENDIX A (continued)

Lab Number	Company	Sample Notes	Date Collected or Received
Gyp-58	Occidental	Sample collected from Doroliver Stack #1 in Section 1 - Center where gypsum is being harvested for re-sale. Gypsum is 15 - 16 years old.	03/11/93
Gyp-59	Occidental	Sample collected from Doroliver Stack #3. Gypsum is 1 to 2 years old.	03/11/93
Gyp-60	Occidental	Sample collected from CTC Stack #2 - Section 2. Gypsum is ~ 30% HH and 70% DH when pumped to stack. Sample collected from stack summit. Stack ~ 5 - 10 years old.	3/11/93
		Phosphate Rock Samples	
Ore-10/1	Occidental	Unconcentrated rock from mine; contains a significant amount of sand.	04/30/91
Ore-10/2	Occidental	Beneficiated ore rock that was being reacted; Gyp-10 is the resultant by-product.	04/30/91

APPENDIX A (continued)

Lab Number	Company	Sample Notes	Date Collected or Received
Ore-14	Farmland	Beneficiated ore rock used to produce OreS-14*. Sample provided by Farmland.	11/07/91
OreS-14*	Farmland	Ore-14 slurry used in reaction chamber. Gyp-14 is the resultant by-product.	11/07/91
Ore-18	Farmland	Ore rock being used to produce OreS-18.	02/03/92
OreS-18	Farmland	Ore-18 slurry used in reaction chamber. Gyp-18 is the resultant by-product.	02/03/92
Ore-19	Royster	Ore rock being used to produce OreS-19.	02/04/92
OreS-19	Royster	Ore-19 slurry used in reaction chamber. Gyp-19 is the resultant by-product.	02/04/92
OreS-21	CF Industries (Plant City)	Ore-21 slurry used in reaction chamber. Gyp-21 is the resultant by-product. Only an OreS sample of ore was collected.	02/04/92
OreS-26	IMC New Wales	Ore-26 slurry used in reaction chamber. Ore slurry collected from "east train "of the reaction line. Gyp-26 is the by-product.	03/27/92

APPENDIX A (continued)

Lab Number	Company	Sample Notes	Date Collected or Received
OreS-31	CF Industries (Plant City)	Ore-31 slurry used in reaction chamber. Gyp-31 is the resultant by-product. Only an OreS sample of ore was collected. Sample provided by CF personnel.	03/27/92
Ore-34	Seminole	Ore rock blend which was being used on the date of collection. Gyp-34 is the resultant by-product produced in the reaction chamber of Phosphoric Acid Plant #4.	06/17/92
OreS-38	Agrico, South Pierce Plant	Ore-38 slurry used in reaction chamber. Gyp-38 is the resultant by-product. Only an OreS sample of ore was collected. Sample provided by Agrico personnel.	06/22/92
OreS-47	U.S. Agrichemicals Fort Meade	Ore-47 slurry used in reaction chamber. Gyp-47 is the resultant by-product. Two bottles collected.	09/29/92
Ore-48	IMC Nichols	Ore rock blend which was being used on the date of collection. Gyp-48 is the resultant by-product produced in the reaction chamber.	01/14/93

APPENDIX A (continued)

Lab Number	Company	Sample Notes	Date Collected or Received
Ore-53	Occidental	Ore rock which was being used at the Suwannee River Complex on the date of collection. Gyp-53 is the DH by-product.	01/15/93
Ore-54	Occidental	Ore rock which was being used at the Swift Creek Complex on the date of collection. Gyp-54 is the HH by-product.	01/15/93
		Miscellaneous Samples	
Gypxl-1	IMC New Wales	Samples of clear, pseudohexagonal crystals growing in zones of cooling water discharge on the north and south flanks of the stack. The crystals are from <1 to ~4 cm inlength and grow in aggregates or "mats" in the zones of discharge above drainage channels.	03/27/92
Filter #1	CF Industries (Plant City)	Segment of unwashed polypropaline weave filter screen ~28 cm x 70 cm. An appreciable amount of filter cake (scale) remained on the filter screen.	06/18/92

APPENDIX A (continued)

Lab Number	Company	Sample Notes	Date Collected or Received
CC-1	U. S. Bureau of Mines	Split spoon core samples of the CC-1well drilled through the IMC P-21 stack. Each core sample is from a five foot segment of the well that has a total depth of 40 feet. Eight core samples provided.	06/18/92
P-47	U.S. Agrichem. Fort Meade	Sample of phosphoric acid produced from OreS-47. Gyp-47 is the resultant by-product.	09/29/92
P-48	IMC Nichols	Sample of phosphoric acid produced from Ore-48. Gyp-48 is the resultant by-product.	01/14/93
P-53(a) & (b)	Occidental	Samples of phosphoric acid produced from Ore-53. Gyp-53 is the resultant by-product. P-53(a) is the #1 Filtrate and P-54(b) is #2 Filtrate produced at the Suwanne River Complex (DH) on this date.	01/15/93
P-54	Occidental	Sample of phosphoric acid produced from Ore-54. P-54 is the #1 Filtrate produced at the Swift Creek (HH) Complex on this date.	01/15/93

APPENDIX A (continued)

Lab Number	Company	Sample Notes	Date Collected or Received
CW-1	IMC Nichols	Filter wash water used to slurry phosphogypsum filtrate from the reaction chamber. Gyp-48 slurried with this water on this date.	01/14/93
CW-2	Occidental	Filter wash water used to slurry dihydrate filtrate from the reaction chamber at the Suwannee River Complex (DH) on this date. Gyp-53 slurried with this water.	01/15/93
CW-3	Occidental	Filter wash water used to slurry dihydrate filterate from the reaction chamber at the Swift Creek Complex (HH) on this date. Gyp-54 slurried with this water.	01/15/93

* **S** appended to **Ore** indicates ore rock slurry. OreS samples are beneficated ore rocks which are usually slurried with cooling pond water. pH of ore slurry is raised to >4 to decrease corrosivity.

APPENDIX B

Radioanalytical Results

APPENDIX B. Radiochemical analyses of bulk phosphogypsum and phosphate rock samples. Replicates of samples have been analyzed when more than one ^{210}Po and ^{238}U activity (measured by α spectrometry) is given for a sample. More than one activity given for radionuclides measured by γ spectrometry (^{234}Th , ^{226}Ra, and ^{210}Pb) are recounts of the same sample unless sub-sample numbers are given. Errors are given at the 1 σ level based on counting statistics only.

Company	Sample ID	^{238}U (^{234}Th by γ) dpm/g	^{226}Ra dpm/g	^{210}Pb dpm/g	^{210}Po dpm/g	$^{210}Pb/^{226}Ra$ Activity	$^{210}Po/^{210}Pb$ Ratios
			Phosphogypsum Samples				
Estech	Gyp-1	3.0±0.3	49.0±0.3	41.2±0.6	43.7±0.7	0.84±0.01	1.06±0.02
U.S Agrichem (Bartow)	Gyp-2	2.4±0.4	64.5±0.4	56.6±0.8	57.9±1.1	0.88±0.01	1.02±0.03
IMC	Gyp-3	6.3±0.4	60.9±0.3	57.2±0.7	55.5±0.8	0.94±0.01	0.97±0.02
Farmland	Gyp-4	5.8±0.4	64.6±0.8	58.1±0.8	58.9±0.9	0.90±0.02	1.01±0.02
IMC (P-21)	Gyp-5/1	8.0±0.5	51.9±0.3	49.4±0.8	51.0±0.7 52.1±0.5	0.95±0.02	1.03±0.02 1.06±0.02
IMC (P-21)	Gyp-5/2	4.9±0.3	41.0±0.2	41.4±0.5	42.3±0.7 42.3±0.6	1.01±0.01	1.02±0.02 1.02±0.02
Royster	Gyp-6(1)	5.1±0.4	41.2±0.3	37.6±0.6	37.7±1.0	0.91±0.02	1.00±0.03
	Gyp-6(2)	4.7±0.4	40.2±0.3	38.2±0.7	37.5±0.6	0.95±0.02	0.98±0.03
	Gyp-6(3)	4.3±0.3	40.3±0.3	38.5±0.7	37.3±0.5	0.96±0.02	0.97±0.02
	Gyp-6(4)	4.7±0.3	40.6±0.3	38.9±0.7	38.1±0.7	0.96±0.02	0.98±0.03
	Gyp-6 (Ave.)	4.7±0.3	40.6±0.5	38.3±0.6	37.7±0.3	0.95±0.02	0.98±0.01

APPENDIX B (continued)

Company	Sample ID	^{238}U (^{234}Th by γ) dpm/g	^{226}Ra dpm/g	^{210}Pb dpm/g	^{210}Po dpm/g	$^{210}Pb/^{226}Ra$ Activity	$^{210}Po/^{210}Pb$ Ratios
Royster	Gyp-6(1&2)	5.1±0.2	40.3±0.2	37.5±0.4	37.3±0.4	0.93±0.01	0.99±0.01
	$^{238}U(\alpha)$	5.3±0.4					
Royster	Gyp-7	9.2±0.4	38.4±0.3	38.4±0.6	39.8±0.6	1.00±0.02	1.04±0.02
Royster	Gyp-8	15.0±0.5	46.9±0.3	45.9±0.7	45.3±0.6	0.98±0.02	0.99±0.02
	$^{238}U(\alpha)$	16.2±0.3					
	$^{238}U(\alpha)$	17.0±0.6					
C. F. Ind. (Bartow)	Gyp-9	4.1±0.4	66.3±0.4	79.6±0.8	56.2±1.0	1.20±0.01	0.71±0.02
Occidental	Gyp-10	1.9±0.2	16.2±0.2	20.6±0.4	21.9±0.4	1.27±0.03	1.06±0.03
		1.7±0.2	16.1±0.2	20.9±0.5		1.30±0.04	
	$^{238}U(\alpha)$	1.7±0.1					
Cargil	Gyp-11	4.0±0.4	57.4±0.3	47.2±0.7	44.9±0.6	0.82±0.01	0.95±0.02
Farmland	Gyp-12	5.9±0.4	46.4±0.3	44.1±0.7	45.3±0.7	0.95±0.01	1.03±0.02
Farmland	Gyp-13	6.0±0.3	44.8±0.2	44.7±0.5	46.2±0.6	1.00±0.01	1.03±0.02
	$^{238}U(\alpha)$	6.4±0.1					
Farmland	Gyp-14	8.1±0.5	48.7±0.3	48.7±0.7	49.0±0.7	1.00±0.02	1.01±0.02

APPENDIX B (continued)

Company	Sample ID	^{238}U (^{234}Th by γ) dpm/g	^{226}Ra dpm/g	^{210}Pb dpm/g	^{210}Po dpm/g	$^{210}Pb/^{226}Ra$ Activity	$^{210}Po/^{210}Pb$ Ratios
Farmland	Gyp-15	5.2±0.3	39.2±0.3	40.3±0.6	36.7±0.6	1.03±0.02	0.91±0.02
Farmland	Gyp-16	2.8±0.4	81.2±0.4	60.9±1.0	58.8±0.7	0.75±0.01	0.97±0.02
Farmland	Gyp-17	7.3±0.5	80.5±0.4	110.0±0.9	105.9±1.6	1.36±0.01	0.97±0.02
Farmland	Gyp-18	12.5±0.5*	53.5±0.3	49.2±0.7	54.3±0.9	0.92±0.01	1.10±0.02
		9.2±0.7	51.6±0.4	48.9±0.9	55.8±0.6	0.95±0.02	1.14±0.02
	$^{238}U(\alpha)$	9.1±0.4					
	$^{238}U(\alpha)$	9.1±0.3					
Royster	Gyp-19	10.9±0.4*	32.7±0.2	34.9±0.5	33.9±0.6	1.07±0.02	0.97±0.02
		10.0±0.5	33.3±0.3	34.5±0.7		1.04±0.02	
	$^{238}U(\alpha)$	9.8±0.3					
IMC (P-21) Profile	Gyp-20(0-2cm)	3.7±0.3	42.1±0.3	42.3±0.7	42.5±0.6	1.00±0.02	1.00±0.02
	Gyp-20(2-5cm)	3.3±0.3	37.8±0.3	38.5±0.7	40.6±0.6	1.02±0.02	1.05±0.02
	Gyp-20(5-8cm)	2.1±0.3	47.9±0.3	47.9±0.3	44.8±0.6	1.05±0.02	0.94±0.01
	Gyp-20(8-15cm)	2.0±0.3	49.4±0.3	45.5±0.8	45.7±0.5	0.92±0.02	1.01±0.02
C. F. Ind. (Plant City)	Gyp-21	9.5±0.6*	57.7±0.4	60.7±0.8	69.1±0.9	1.05±0.02	1.14±0.02
		11.1±0.8	59.6±0.5	59.7±1.0	71.4±0.9	1.00±0.02	1.18±0.02
	$^{238}U(\alpha)$	10.0±0.2			70.6±0.5		1.16±0.02

	10 Feb 93 Analysis				62.8±0.5		1.03±0.02

APPENDIX B (continued)

Company	Sample ID	^{238}U (^{234}Th by γ) dpm/g	^{226}Ra dpm/g	^{210}Pb dpm/g	^{210}Po dpm/g	$^{210}Pb/^{226}Ra$ Activity	$^{210}Po/^{210}Pb$ Ratios
C. F. Ind. (Plant City)	Gyp-22	7.5±0.4*	54.6±0.3	50.3±0.6	57.9±0.9	0.92±0.01	1.15±0.02
		7.1±0.6	56.1±0.4	52.2±0.8		0.93±0.02	
C. F. Ind. (Plant City)	Gyp-23	5.0±0.4*	59.1±0.4	53.2±0.7	35.8±0.6	0.90±0.01	0.67±0.02
		7.4±0.7	60.8±0.5	55.5±0.9	38.6±0.6	0.91±0.02	0.73±0.01
C. F. Ind. (Plant City)	Gyp-24	4.0±0.4*	55.4±0.3	43.8±0.7	45.4±0.7	0.79±0.01	1.04±0.02
					38.9±0.5		0.61±0.01
					39.9±0.5		0.64±0.01
C. F. Ind. (Plant City)	Gyp-25	3.6±0.3	47.1±0.3	40.1±0.7	39.6±0.5	0.85±0.02	0.99±0.02
					39.8±0.6		0.99±0.02
	30 Jan 93 Po Analysis				38.1±0.4		0.95±0.02
					36.9±0.3		0.92±0.02
	26 Jun 93 Po Analysis				36.7±0.4		0.92±0.01
IMC New Wales	Gyp-26	15.3±0.4*	44.2±0.2	50.6±0.5	51.8±0.4	1.14±0.01	1.02±0.01
		15.4±0.7	44.5±0.4	50.8±0.8		1.14±0.02	
	$^{238}U(\alpha)$	15.5±0.2					
IMC New Wales	Gyp-27	3.0±0.2	39.1±0.2	37.4±0.4	36.7±0.4	0.96±0.01	0.98±0.01
IMC New	Gyp-28	3.6±0.4	56.5±0.3	50.7±0.7	52.8±0.6	0.90±0.01	1.04±0.02

Wales

APPENDIX B (continued)

Company	Sample ID	^{238}U (^{234}Th by γ) dpm/g	^{226}Ra dpm/g	^{210}Pb dpm/g	^{210}Po dpm/g	$^{210}Pb/^{226}Ra$ Activity	$^{210}Po/^{210}Pb$ Ratios
IMC New Wales	Gyp-29	8.2±0.4	49.4±0.3	51.7±0.7	48.7±0.6	1.05±0.02	0.94±0.02
IMC New Wales	Gyp-30	9.8±0.5*	46.4±0.4	51.0±0.7	38.8±0.4	1.10±0.02	0.76±0.01
		8.8±0.5	45.0±0.3	51.0±0.7		1.13±0.02	
	$^{238}U(\alpha)$	9.6±0.2					
	$^{238}U(\alpha)$	9.0±0.3					
C. F. Ind.	Gyp-31	10.8±0.5*	72.2±0.4	62.2±0.8	72.6±0.6	0.86±0.01	1.17±0.02
		11.1±0.7	70.4±0.4	63.1±0.9		0.90±0.01	
	$^{238}U(\alpha)$	10.7±0.1					
Seminole	Gyp-32	3.7±0.2	60.0±0.3	44.3±0.5	45.5±0.5	0.74±0.01	1.03±0.02
Seminole	Gyp-33	7.3±0.3*	49.0±0.2	51.3±0.4	41.1±0.5	1.05±0.01	0.80±0.01
		6.1±0.5	48.7±0.4	53.1±0.8		1.09±0.01	
Seminole	Gyp-34	9.3±0.3*	57.8±0.3	54.7±0.5	51.9±0.6	0.95±0.01	0.95±0.01
		9.3±0.6	55.3±0.4	57.0±0.8		1.03±0.02	
	$^{238}U(\alpha)$	10.6±0.4					
Seminole	Gyp-35	8.0±0.3*	58.0±0.3	55.3±0.5	58.4±0.8	0.95±0.01	1.06±0.02
		7.4±0.6	57.5±0.4	56.6±0.9		0.98±0.02	

APPENDIX B (continued)

Company	Sample ID	^{238}U (^{234}Th by γ) dpm/g	^{226}Ra dpm/g	^{210}Pb dpm/g	^{210}Po dpm/g	$^{210}Pb/^{226}Ra$ Activity	$^{210}Po/^{210}Pb$ Ratios
Seminole	Gyp-36	9.2±0.4*	63.3±0.3	55.4±0.5	61.8±0.9	0.88±0.01	1.12±0.02
		10.5±0.7	62.3±0.4	55.7±0.8		0.89±0.01	
Seminole	Gyp-37	3.7±0.2	79.9±0.3	54.9±0.5	56.3±0.7	0.69±0.01	1.03±0.02
Agrico	Gyp-38	21.8±0.6*	44.8±0.3	50.1±0.8	56.5±0.6	1.11±0.02	1.13±0.02
		19.4±0.5	49.9±0.2	46.5±0.6		0.93±0.01	
	$^{238}U(\alpha)$	24.4±0.5					
Agrico	Gyp-39	11.9±0.3*	31.6±0.2	36.9±0.3	26.1±0.7	1.17±0.01	0.71±0.01
		10.2±0.5	31.0±0.2	37.2±0.6		1.20±0.02	
Agrico	Gyp-40	8.3±0.4	49.0±0.3	44.0±0.5	72.4±0.7	0.90±0.01	1.65±0.02
Agrico	Gyp-41	5.2±0.3	59.7±0.3	49.5±0.6	51.7±0.6	0.87±0.01	1.04±0.02
Agrico	Gyp-42	4.2±0.3	64.8±0.3	53.6±0.6	53.8±0.9	0.83±0.01	1.00±0.02
U. S Agrichem	Gyp-43	2.7±0.3	65.7±0.2	57.1±0.5	56.4±1.0	0.87±0.01	0.99±0.02
	$^{238}U(\alpha)$	2.8±0.1					
U. S Agrichem	Gyp-44B	<21.6±0.8	57.8±0.3	69.6±0.9	58.4±0.7	1.20±0.02	0.84±0.01
	Gyp-44B	22.5±0.8	57.3±0.3	67.5±0.9		1.18±0.02	

APPENDIX B (continued)

Company	Sample ID	^{238}U (^{234}Th by γ) dpm/g	^{226}Ra dpm/g	^{210}Pb dpm/g	^{210}Po dpm/g	$^{210}Pb/^{226}Ra$ Activity	$^{210}Po/^{210}Pb$ Ratios
U. S Agrichem	Gyp-45	4.9±0.4	40.4±0.2	49.2±0.6	40.7±0.6	1.22±0.02	0.83±0.02
U. S Agrichem	Gyp-46	6.6±0.5	57.9±0.3	49.4±0.8	49.6±0.6	0.85±0.01	1.00±0.02
	Gyp-46(1)	4.7±0.5	53.1±0.2	50.8±0.7		0.96±0.01	
	Gyp-46(2)	3.9±0.4	54.5±0.2	49.8±0.6		0.91±0.01	
	Gyp-46(3)	4.9±0.4	53.1±0.2	50.8±0.6		0.96±0.01	
	Gyp-46(4)	4.8±0.5	54.7±0.2	51.3±0.7		0.94±0.01	
	Gyp-46(5)	4.8±0.5	54.4±0.2	50.7±0.7		0.93±0.01	
U. S Agrichem	Gyp-47B	18.2±0.6	66.2±0.3	57.2±0.6	59.1±0.5	0.86±0.01	1.03±0.02
	Gyp-47B	18.8±0.8	64.9±0.4	55.4±0.9		0.85±0.01	
	$^{238}U(\alpha)$	19.8±0.7					
	$^{238}U(\alpha)$	17.9±0.6					
IMC Nichols	Gyp-48	17.4±0.7*	68.1±0.3	56.5±0.8	63.1±0.9	0.83±0.01	1.11±0.02
		18.0±0.8	68.0±0.3	56.6±0.8		0.83±0.01	
	$^{238}U(\alpha)$	17.3±0.4					
IMC Nichols	Gyp-49	8.9±0.6	55.9±0.2	54.7±0.7	47.5±0.6	0.98±0.01	0.87±0.02
		7.4±0.6	55.5±0.3	54.7±0.8		0.99±0.02	
IMC Nichols	Gyp-50	6.8±0.5	46.0±0.2	51.3±0.7	47.2±0.5	1.12±0.01	0.92±0.01

APPENDIX B (continued)

Company	Sample ID	^{238}U (^{234}Th by γ) dpm/g	^{226}Ra dpm/g	^{210}Pb dpm/g	^{210}Po dpm/g	$^{210}Pb/^{226}Ra$ Activity	$^{210}Po/^{210}Pb$ Ratios
IMC Nichols	Gyp-51	5.4±0.4	53.3±0.2	35.0±0.5	55.0±0.7	0.66±0.01	1.57±0.02
IMC Nichols	Gyp-52	6.9±0.8	74.7±0.3	77.0±1.2	56.1±0.6	1.03±0.02	0.73±0.02
Occidental	Gyp-53	7.5±0.3	36.0±0.2	27.9±0.4	30.2±0.5	0.78±0.01	1.08±0.02
		7.6±0.5	35.7±0.3	27.8±0.6		0.78±0.02	
	$^{238}U(\alpha)$	7.5±0.2					
Occidental	Gyp-54	<27.7±0.5	34.7±0.2	33.2±0.5	34.0±0.9	0.96±0.02	1.02±0.03
		26.5±0.5	34.4±0.2	32.2±0.5		0.94±0.02	
	$^{238}U(\alpha)$	28.1±0.7					
Occidental	Gyp-55	8.6±0.4	34.7±0.2	33.2±0.5	24.6±0.6	1.12±0.02	0.85±0.02
Occidental	Gyp-56	8.9±0.4	19.4±0.1	21.3±0.5	21.3±0.3	1.10±0.02	1.00±0.03
Occidental	Gyp-57	9.1±0.4	19.4±0.2	23.0±0.5	23.0±0.3	1.19±0.02	1.00±0.02
	$^{238}U(\alpha)$	9.0±0.7					
Occidental	Gyp-58	2.0±0.1	26.7±0.1	27.3±0.4	25.7±0.3	1.02±0.02	0.94±0.02
Occidental	Gyp-59	3.4±0.3	25.2±0.1	24.9±0.4	24.4±0.3	0.99±0.02	0.98±0.02

Occidental	Gyp-60	1.4±0.2	21.8±0.2	24.0±0.5	25.3±0.4	1.10±0.02	1.05±0.03

APPENDIX B (continued)

Company	Sample ID	^{238}U (^{234}Th by γ) dpm/g	^{226}Ra dpm/g	^{210}Pb dpm/g	^{210}Po dpm/g	$^{210}Pb/^{226}Ra$ Activity	$^{210}Po/^{210}Pb$ Ratios
CF Ind. (Bartow)	Gyp-DL3(1)	2.0±0.2	54.2±0.2	44.7±0.4	-	0.82±0.01	-
	Gyp-DL3(2)	2.1±0.2	54.4±0.3	46.8±0.5	-	0.86±0.01	-
	Gyp-DL3(3)	2.9±0.2	53.7±0.2	46.4±0.4	-	0.86±0.01	-
	Gyp-DL3(4)	3.1±0.2	54.2±0.2	47.2±0.5	-	0.87±0.01	-
	Gyp-DL3 Vial	1.6±0.3	53.6±0.5	45.5±1.0	-	0.87±0.01	-
	Gyp-DL3 Ave.	2.3±0.2	54.0±0.3	46.1±0.6	-	0.86±0.01	-
Phosphogypsum Samples from U. S. Bureau of Mines Well							
IMC (P-21)	CC-1 0-5 Ft.	2.2±0.2	55.0±0.3	48.5±0.5	54.2±0.7	0.88±0.01	1.11±0.02
IMC (P-21)	CC-1 5-10 Ft.	3.9±0.2	58.6±0.3	53.2±0.5	58.2±0.5	0.91±0.01	1.09±0.01
IMC (P-21)	CC-1 10-15 Ft.	5.3±0.3	55.0±0.3	53.9±0.5	62.6±0.5	0.98±0.01	1.16±0.01
IMC (P-21)	CC-1 15-20 Ft.	4.0±0.2	56.2±0.3	55.3±0.5	54.7±0.7	0.98±0.01	0.99±0.02
IMC (P-21)	CC-1 20-25 Ft.	3.3±0.2	59.9±0.2	55.9±0.5	59.8±0.4	0.93±0.01	1.07±0.01
IMC (P-21)	CC-1 25-30 Ft.	3.2±0.2	62.1±0.2	56.2±0.4	63.9±0.4	0.90±0.01	1.14±0.01
IMC (P-21)	CC-1 30-35 Ft.	4.7±0.4	58.8±0.2	63.8±0.8	61.3±0.7	1.09±0.01	0.96±0.02

IMC (P-21)	CC-1 35-40 Ft.	24.6±0.3	30.3±0.2	30.9±0.3	34.0±0.4	1.02±0.01	1.10±0.02

APPENDIX B (continued)

Company	Sample ID	^{238}U (^{234}Th by γ) dpm/g	^{226}Ra dpm/g	^{210}Pb dpm/g	^{210}Po dpm/g	$^{210}Pb/^{226}Ra$ Activity	$^{210}Po/^{210}Pb$ Ratios
			Phosphate Rock Samples				
Occidental	Ore-10/1	14.5±0.3	13.8±0.1	14.4±0.4	14.3±0.3	1.05±0.03	0.99±0.04
Occidental	Ore-10/2	34.7±0.5	35.3±0.2	35.6±0.6	36.8±1.3	1.01±0.02	1.03±0.04
Farmland	Ore-14	81.1±0.7	87.7±0.3	88.2±1.0	86.3±2.1	1.01±0.01	0.98±0.03
					86.2±1.2		0.98±0.02
					79.2±2.1		0.90±0.03
Farmland	OreS-14	83.2±0.6	89.2±0.3	86.9±0.8	87.9±2.4	0.97±0.01	1.01±0.03
Farmland	Ore-18	74.4±0.6*	79.8±0.3	75.3±1.1	75.6±1.3	0.94±0.01	1.00±0.02
					77.5±1.2		1.03±0.02
		80.0±0.8	77.9±0.2	75.6±0.8		0.97±0.01	
Farmland	OreS-18	68.8±0.8*	80.9±0.3	80.3±1.1	77.8±1.4	0.99±0.01	0.97±0.02
		84.5±1.2	79.7±0.3	79.9±1.1	82.8±2.5	1.00±0.01	1.04±0.03
	$^{238}U(\alpha)$	84.3±2.0					
Royster	Ore-19	44.2±0.6*	52.9±0.3	52.9±1.0	52.3±1.7	1.00±0.02	0.99±0.04
					55.0±2.3		1.04±0.05
					53.7±0.5		1.02±0.02

APPENDIX B (continued)

Company	Sample ID	^{238}U (^{234}Th by γ) dpm/g	^{226}Ra dpm/g	^{210}Pb dpm/g	^{210}Po dpm/g	$^{210}Pb/^{226}Ra$ Activity	$^{210}Po/^{210}Pb$ Ratios
Royster	OreS-19	61.3±0.7	56.4±0.2	56.2±0.7	57.8±0.5	1.00±0.02	1.03±0.02
	$^{238}U(\alpha)$	60.4±1.2			54.9±1.0		0.98±0.02
C. F. Ind. (Plant City)	OreS-21	102.6±1.1	98.8±0.4	100.2±1.3	93.4±2.1	1.01±0.01	0.93±0.02
		102.0±1.3	99.1±0.4	97.1±1.3	97.8±1.6	0.99±0.01	1.01±0.02
	$^{238}U(\alpha)$	102.6±2.5					
	$^{238}U(\alpha)$	106.0±2.2					
IMC New Wales	OreS-26	75.2±0.7*	94.3±0.3	88.8±0.9	88.5±1.6	0.94±0.01	1.00±0.02
		93.4±1.3	91.2±0.4	91.2±1.3		1.00±0.01	
	$^{238}U(\alpha)$	97.2±1.2					
C. F. Ind. (Plant City)	OreS-31	118.8±1.4	113.7±0.4	109.9±1.4	110.1±1.6	0.97±0.01	1.00±0.02
	$^{238}U(\alpha)$	111.6±1.1					
Seminole	Ore-34	73.6±0.4*	94.7±0.2	86.7±0.5	87.4±0.8	0.92±0.01	1.01±0.01
		94.5±1.3*	91.7±0.4	91.4±1.3		1.00±0.01	
	$^{238}U(\alpha)$	89.6±2.4					
Agrico	OreS-38	77.8±0.7	69.8±0.2	80.9±0.8	87.4±0.8	0.92±0.01	1.01±0.01
	$^{238}U(\alpha)$	81.0±2.1					

APPENDIX B (continued)

Company	Sample ID	^{238}U (^{234}Th by γ) dpm/g	^{226}Ra dpm/g	^{210}Pb dpm/g	^{210}Po dpm/g	$^{210}Pb/^{226}Ra$ Activity	$^{210}Po/^{210}Pb$ Ratios
U.S. Agrichem	OreS-47	87.2±0.8	55.0±0.2	59.4±0.8	61.2±1.1	1.08±0.02	1.03±0.02
	$^{238}U(\alpha)$	90.3±1.6					
IMC Nichols	Ore-48	111.7±1.4	97.7±0.4	110.1±1.6	102.5±1.2	1.13±0.02	0.93±0.02
$^{238}U(\alpha)$		117.1±2.2					
Occidental	Ore-53	57.8±0.7	52.0±0.2	58.9±0.7	52.6±1.0	1.01±0.01	0.89±0.02
	$^{238}U(\alpha)$	57.9±1.6					
Occidental	Ore-54	58.9±1.0	53.0±0.3	56.7±1.0	52.0±1.2	1.07±0.02	0.92±0.03
	$^{238}U(\alpha)$	63.3±1.0					

* Activity measured and calculated prior to development of absorption correction for ^{234}Th γ.

APPENDIX C

Chemical Compositions

FLORIDA STATE/BURNETT

GYP 46
41.841

ELEMENT			CONCENTRATION
NA	%		0.411
K	%		0.175
CA	%		17.191
MG	%		0.008
FE1	%		0.083
AL	%		0.083
SI	%	<	0.628
TI	%		0.022
P	%		0.292
SR	PPM		638.661
BA	%		0.007
V	PPM	<	209.205
CR	PPM	<	1.674
MN	%		0.001
CO	PPM	<	0.837
NI	PPM		5.063
CU	PPM	<	4.184
MO	PPM	<	41.841
PB	PPM		16.611
ZN	PPM	<	4.184
CD	PPM	<	4.184
AG	PPM	<	1.674
AU	PPM	<	3.347
AS	PPM	<	20.920
SB	PPM	<	25.105
BI	PPM	<	83.682
U	PPM	<	2092.050
TE	PPM	<	41.841
SN	PPM	<	4.184
W	PPM	<	1004.184
LI	PPM	<	1.674
BE	PPM	<	0.418
B	PPM	<	334.728
ZR	PPM		6.234
LA	PPM		109.247
CE	PPM	<	8.368
TH	PPM	<	125.523
F	%		0.424
SO4	%		48.05

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FSU-1
98.135

ELEMENT			CONCENTRATION
NA	%		0.034
K	%		0.269
CA	%		2.606
MG	%		0.053
FE1	%		7.937
AL	%		2.324
SI	%	<	1.472
TI	%		0.641
P	%		6.879
SR	PPM		1045.040
BA	%		0.118
V	PPM	<	490.675
CR	PPM		115.799
MN	%		0.009
CO	PPM	<	1.963
NI	PPM		41.217
CU	PPM		307.850
MO	PPM		221.393
PB	PPM		517.073
ZN	PPM		199.508
CD	PPM		15.309
AG	PPM		32.090
AU	PPM	<	7.851
AS	PPM		181.648
SB	PPM	<	58.881
BI	PPM	<	196.270
U	PPM	<	4906.750
TE	PPM	<	98.135
SN	PPM		27.380
W	PPM	<	2355.240
LI	PPM	<	3.925
BE	PPM		4.514
B	PPM	<	785.080
ZR	PPM		170.559
LA	PPM		2455.534
CE	PPM		3597.727
TH	PPM	<	294.405
F	%		1.00

CARTER HULL / FLORIDA STATE UNIVERSITY

FSU-2
50.05

ELEMENT			CONCENTRATION
NA	%		0.016
K	%		0.113
CA	%		0.250
MG	%		0.011
FE1	%		0.764
AL	%		0.246
SI	%	<	0.751
TI	%		0.428
P	%		0.310
SR	PPM		42.693
BA	%		0.007
V	PPM	<	250.250
CR	PPM		14.314
MN	%		0.019
CO	PPM	<	1.001
NI	PPM	<	5.005
CU	PPM		15.866
MO	PPM	<	50.050
PB	PPM		22.172
ZN	PPM		20.020
CD	PPM	<	5.005
AG	PPM		4.254
AU	PPM	<	4.004
AS	PPM	<	25.025
SB	PPM	<	30.030
BI	PPM	<	100.100
U	PPM	<	2502.500
TE	PPM	<	50.050
SN	PPM	<	5.005
W	PPM	<	1201.200
LI	PPM		2.052
BE	PPM	<	0.500
B	PPM	<	400.400
ZR	PPM		36.436
LA	PPM		85.535
CE	PPM		131.431
TH	PPM	<	150.150
F	%		0.094
SO4	%		0.008

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FSU-3
49.95

ELEMENT			CONCENTRATION
NA	%		0.015
K	%		0.123
CA	%		0.365
MG	%		0.015
FE1	%		1.081
AL	%		0.329
SI	%	<	0.749
TI	%		0.393
P	%		0.571
SR	PPM		89.111
BA	%		0.011
V	PPM	<	249.750
CR	PPM		19.231
MN	%		0.018
CO	PPM	<	0.999
NI	PPM		6.294
CU	PPM		27.872
MO	PPM	<	49.950
PB	PPM		41.209
ZN	PPM		29.421
CD	PPM	<	4.995
AG	PPM		4.695
AU	PPM	<	3.996
AS	PPM	<	24.975
SB	PPM	<	29.970
BI	PPM	<	99.900
U	PPM	<	2497.500
TE	PPM	<	49.950
SN	PPM	<	4.995
W	PPM	<	1198.800
LI	PPM	<	1.998
BE	PPM		0.549
B	PPM	<	399.600
ZR	PPM		39.111
LA	PPM		175.225
CE	PPM		279.970
TH	PPM	<	149.850
F	%		0.150
SO4	%		0.004

CARTER HULL / FLORIDA STATE UNIVERSITY

FSU-4
49.87

ELEMENT			CONCENTRATION
NA	%		0.016
K	%		0.013
CA	%		20.720
MG	%		0.005
FE1	%		0.111
AL	%		0.081
SI	%	<	0.748
TI	%		0.047
P	%		0.245
SR	PPM		603.477
BA	%		0.008
V	PPM	<	249.350
CR	PPM		3.142
MN	%		0.002
CO	PPM	<	0.997
NI	PPM	<	4.987
CU	PPM		5.436
MO	PPM	<	49.870
PB	PPM		10.722
ZN	PPM	<	4.987
CD	PPM	<	4.987
AG	PPM		3.391
AU	PPM	<	3.990
AS	PPM	<	24.935
SB	PPM	<	29.922
BI	PPM	<	99.740
U	PPM	<	2493.500
TE	PPM	<	49.870
SN	PPM	<	4.987
W	PPM	<	1196.880
LI	PPM	<	1.995
BE	PPM	<	0.499
B	PPM	<	398.960
ZR	PPM		30.072
LA	PPM		105.675
CE	PPM		58.348
TH	PPM	<	149.610
F	%		0.270
SO4	%		46.62

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FSU-5
49.652

ELEMENT			CONCENTRATION
NA	%		0.017
K	%		0.014
CA	%		21.712
MG	%		0.006
FE1	%		0.122
AL	%		0.077
SI	%	<	0.745
TI	%		0.049
P	%		0.243
SR	PPM		626.608
BA	%		0.008
V	PPM	<	248.260
CR	PPM		3.923
MN	%		0.002
CO	PPM		1.589
NI	PPM	<	4.965
CU	PPM		5.909
MO	PPM		52.929
PB	PPM		16.882
ZN	PPM	<	4.965
CD	PPM	<	4.965
AG	PPM		5.809
AU	PPM		5.462
AS	PPM	<	24.826
SB	PPM	<	29.791
BI	PPM	<	99.304
U	PPM	<	2482.600
TE	PPM	<	49.652
SN	PPM	<	4.965
W	PPM	<	1191.648
LI	PPM	<	1.986
BE	PPM	<	0.497
B	PPM	<	397.216
ZR	PPM		26.514
LA	PPM		99.403
CE	PPM		85.997
TH	PPM	<	148.956
F	%		0.293
SO4	%		48.53

CARTER HULL / FLORIDA STATE UNIVERSITY

FSU-6
96.413

ELEMENT			CONCENTRATION
NA	%		0.028
K	%		0.055
CA	%		15.514
MG	%		0.016
FE1	%		0.373
AL	%		0.292
SI	%	<	1.446
TI	%		0.158
P	%		0.383
SR	PPM		537.213
BA	%		0.014
V	PPM	<	482.065
CR	PPM		10.605
MN	%		0.006
CO	PPM		2.121
NI	PPM	<	9.641
CU	PPM		14.848
MO	PPM	<	96.413
PB	PPM		33.648
ZN	PPM		19.765
CD	PPM	<	9.641
AG	PPM		10.798
AU	PPM		9.159
AS	PPM	<	48.207
SB	PPM	<	57.848
BI	PPM	<	192.826
U	PPM	<	4820.650
TE	PPM	<	96.413
SN	PPM	<	9.641
W	PPM	<	2313.912
LI	PPM	<	3.857
BE	PPM	<	0.964
B	PPM	<	771.304
ZR	PPM		42.325
LA	PPM		140.088
CE	PPM		174.893
TH	PPM	<	289.239
F	%		0.548
SO4	%		33.70

FLORIDA STATE/BURNETT

RES 1
43.26

ELEMENT			CONCENTRATION
NA	%		0.042
K	%		0.171
CA	%		6.857
MG	%		0.014
FE1	%		0.707
AL	%		0.562
SI	%	<	0.649
TI	%		0.227
P	%		0.339
SR	PPM		231.960
BA	%		0.017
V	PPM	<	216.300
CR	PPM		18.775
MN	%		0.009
CO	PPM	<	0.865
NI	PPM		8.912
CU	PPM	<	4.326
MO	PPM	<	43.260
PB	PPM		39.064
ZN	PPM		29.633
CD	PPM	<	4.326
AG	PPM	<	1.730
AU	PPM	<	3.461
AS	PPM	<	21.630
SB	PPM	<	25.956
BI	PPM	<	86.520
U	PPM	<	2163.000
TE	PPM	<	43.260
SN	PPM	<	4.326
W	PPM	<	1038.240
LI	PPM	<	1.730
BE	PPM	<	0.433
B	PPM	<	346.080
ZR	PPM		53.642
LA	PPM		293.260
CE	PPM		415.945
TH	PPM	<	129.780
F	%		1.38
SO4	%		0.874

FLORIDA STATE/BURNETT

RES 2
44.723

ELEMENT			CONCENTRATION
NA	%		0.044
K	%		0.147
CA	%		11.039
MG	%		0.010
FE1	%		0.606
AL	%		0.660
SI	%	<	0.671
TI	%		0.254
P	%		0.273
SR	PPM		207.336
BA	%		0.017
V	PPM	<	223.615
CR	PPM		19.499
MN	%		0.010
CO	PPM	<	0.894
NI	PPM		9.347
CU	PPM		18.694
MO	PPM	<	44.723
PB	PPM		40.832
ZN	PPM		25.492
CD	PPM	<	4.472
AG	PPM		2.013
AU	PPM	<	3.578
AS	PPM		23.345
SB	PPM	<	26.834
BI	PPM	<	89.446
U	PPM	<	2236.150
TE	PPM	<	44.723
SN	PPM	<	4.472
W	PPM	<	1073.352
LI	PPM	<	1.789
BE	PPM	<	0.447
B	PPM	<	357.784
ZR	PPM		46.288
LA	PPM		302.149
CE	PPM		335.422
TH	PPM	<	134.169
F	%		3.11
SO4	%		1.09

FLORIDA STATE/BURNETT

RES 3
43.38

ELEMENT			CONCENTRATION
NA	%		0.044
K	%		0.156
CA	%		8.129
MG	%		0.012
FE1	%		0.687
AL	%		0.621
SI	%	<	0.651
TI	%		0.241
P	%		0.319
SR	PPM		431.457
BA	%		0.017
V	PPM	<	216.900
CR	PPM		20.822
MN	%		0.010
CO	PPM		0.868
NI	PPM		9.283
CU	PPM		17.959
MO	PPM	<	43.380
PB	PPM		44.117
ZN	PPM		29.542
CD	PPM	<	4.338
AG	PPM		3.080
AU	PPM	<	3.470
AS	PPM		31.711
SB	PPM	<	26.028
BI	PPM	<	86.760
U	PPM	<	2169.000
TE	PPM	<	43.380
SN	PPM	<	4.338
W	PPM	<	1041.120
LI	PPM	<	1.735
BE	PPM	<	0.434
B	PPM	<	347.040
ZR	PPM		18.176
LA	PPM		279.584
CE	PPM		335.848
TH	PPM	<	130.140
F	%		3.15
SO4	%		1.22

FLORIDA STATE/BURNETT

RES 4
37.481

ELEMENT			CONCENTRATION
NA	%		0.070
K	%		0.148
CA	%		10.279
MG	%		0.017
FE1	%		0.741
AL	%		0.860
SI	%	<	0.562
TI	%		0.242
P	%		0.392
SR	PPM		756.591
BA	%		0.027
V	PPM	<	187.405
CR	PPM		24.625
MN	%		0.010
CO	PPM		2.736
NI	PPM		14.280
CU	PPM		22.414
MO	PPM		37.668
PB	PPM		49.362
ZN	PPM		46.064
CD	PPM	<	3.748
AG	PPM	<	1.499
AU	PPM	<	2.998
AS	PPM		33.920
SB	PPM	<	22.489
BI	PPM	<	74.962
U	PPM	<	1874.050
TE	PPM	<	37.481
SN	PPM	<	3.748
W	PPM	<	899.544
LI	PPM		2.399
BE	PPM		0.487
B	PPM	<	299.848
ZR	PPM		13.418
LA	PPM		316.265
CE	PPM		515.289
TH	PPM	<	112.443
F	%		1.63
SO4	%		2.20

FLORIDA STATE/BURNETT

RES 5
44.177

ELEMENT			CONCENTRATION
NA	%		0.055
K	%		0.175
CA	%		6.904
MG	%		0.021
FE1	%		0.847
AL	%		0.620
SI	%	<	0.663
TI	%		0.223
P	%		0.432
SR	PPM		443.802
BA	%		0.020
V	PPM	<	220.885
CR	PPM		24.386
MN	%		0.011
CO	PPM		3.269
NI	PPM		13.783
CU	PPM		21.382
MO	PPM	<	44.177
PB	PPM		45.105
ZN	PPM		1981.824
CD	PPM	<	4.418
AG	PPM		3.623
AU	PPM	<	3.534
AS	PPM	<	22.088
SB	PPM	<	26.506
BI	PPM	<	88.354
U	PPM	<	2208.850
TE	PPM	<	44.177
SN	PPM	<	4.418
W	PPM	<	1060.248
LI	PPM		3.092
BE	PPM		0.618
B	PPM	<	353.416
ZR	PPM		42.322
LA	PPM		296.339
CE	PPM		526.192
TH	PPM	<	132.531
F	%		2.41
SO4	%		1.28

FLORIDA STATE/BURNETT

RES 6
36.652

ELEMENT			CONCENTRATION
NA	%		0.055
K	%		0.171
CA	%		9.886
MG	%		0.020
FE1	%		0.729
AL	%		0.671
SI	%	<	0.550
TI	%		0.289
P	%		0.399
SR	PPM		439.164
BA	%		0.022
V	PPM	<	183.260
CR	PPM		20.892
MN	%		0.010
CO	PPM		3.299
NI	PPM		10.482
CU	PPM		18.033
MO	PPM		66.890
PB	PPM		40.500
ZN	PPM		29.468
CD	PPM	<	3.665
AG	PPM		7.880
AU	PPM	<	2.932
AS	PPM		26.243
SB	PPM	<	21.991
BI	PPM	<	73.304
U	PPM	<	1832.600
TE	PPM	<	36.652
SN	PPM		14.771
W	PPM	<	879.648
LI	PPM		3.299
BE	PPM		0.513
B	PPM	<	293.216
ZR	PPM		70.079
LA	PPM		303.405
CE	PPM		561.985
TH	PPM		110.689
F	%		1.75
SO4	%		1.37

FLORIDA STATE/BURNETT

RES 7
121.065

ELEMENT			CONCENTRATION
NA	%		0.031
K	%		0.282
CA	%		0.657
MG	%		0.024
FE1	%		4.099
AL	%		0.952
SI	%	<	1.816
TI	%		0.341
P	%		2.609
SR	PPM		250.847
BA	%		0.040
V	PPM	<	605.325
CR	PPM		73.365
MN	%		0.009
CO	PPM	<	2.421
NI	PPM		39.104
CU	PPM		116.828
MO	PPM	<	121.065
PB	PPM		208.353
ZN	PPM		129.176
CD	PPM		20.097
AG	PPM	<	4.843
AU	PPM	<	9.685
AS	PPM		80.387
SB	PPM	<	72.639
BI	PPM	<	242.130
U	PPM	<	6053.250
TE	PPM	<	121.065
SN	PPM		51.695
W	PPM	<	2905.560
LI	PPM	<	4.843
BE	PPM		2.058
B	PPM	<	968.520
ZR	PPM	<	12.107
LA	PPM		684.138
CE	PPM		1166.824
TH	PPM	<	363.195
F			INSUFFICIENT SAMPLE
SO4	%		2.23

FLORIDA STATE/BURNETT

RES 8
42.531

ELEMENT			CONCENTRATION
NA	%		0.010
K	%		0.129
CA	%		0.178
MG	%		0.008
FE1	%		1.089
AL	%		0.324
SI	%	<	0.638
TI	%		0.347
P	%		0.393
SR	PPM		62.776
BA	%		0.010
V	PPM	<	212.655
CR	PPM		21.393
MN	%		0.018
CO	PPM	<	0.851
NI	PPM		6.890
CU	PPM		30.792
MO	PPM	<	42.531
PB	PPM		51.335
ZN	PPM		22.159
CD	PPM		10.080
AG	PPM	<	1.701
AU	PPM	<	3.402
AS	PPM	<	21.265
SB	PPM	<	25.519
BI	PPM	<	85.062
U	PPM	<	2126.550
TE	PPM	<	42.531
SN	PPM	<	4.253
W	PPM	<	1020.744
LI	PPM	<	1.701
BE	PPM		0.553
B	PPM	<	340.248
ZR	PPM	<	4.253
LA	PPM		158.343
CE	PPM		259.014
TH	PPM	<	127.593
F	%		0.110
SO4	%		0.605

RES 9
42.633

ELEMENT			CONCENTRATION
NA	%		0.050
K	%		0.162
CA	%		0.171
MG	%		0.027
FE1	%		1.097
AL	%		0.307
SI	%	<	0.639
TI	%		0.398
P	%		0.468
SR	PPM		62.202
BA	%		0.006
V	PPM	<	213.165
CR	PPM		35.897
MN	%		0.018
CO	PPM		9.720
NI	PPM		25.281
CU	PPM		51.330
MO	PPM		114.512
PB	PPM		108.245
ZN	PPM		32.401
CD	PPM		7.376
AG	PPM	<	1.705
AU	PPM	<	3.411
AS	PPM	<	21.316
SB	PPM	<	25.580
BI	PPM	<	85.266
U	PPM	<	2131.650
TE	PPM	<	42.633
SN	PPM	<	4.263
W	PPM	<	1023.192
LI	PPM		13.600
BE	PPM		1.151
B	PPM	<	341.064
ZR	PPM	<	4.263
LA	PPM		141.627
CE	PPM		232.904
TH	PPM	<	127.899
F	%		0.075
SO4	%		0.694