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Assessment of Environmental Impacts Associated With Phosphogypsum in Florida

By Alexander May and John W. Sweeney

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In its role to provide technology to prevent or limit adverse environmental impacts associated with mining or minerals processing, the Bureau of Mines has conducted research at its Tuscaloosa Research Center to assess the environmental impacts of phosphogypsum produced by the Florida phosphate industry. Over the years, stockpiles containing 335 million tons of phosphogypsum have accumulated and the industry continues to generate an additional 33 million tons a year. Samples from approximately 1,000 feet of drill core, obtained from nine stockpiles were characterized using chemical, X-ray diffraction, emission spectrographic, radiological, and physical means. The data developed indicated that phosphogypsum is not a corrosive or toxic hazardous waste as defined by Environmental Protection Agency criteria. Radium concentrations averaged 21 picocuries per gram and its content was inversely related to particle sizes. Thirty-nine elements were detected in phosphogypsum; concentrations of these elements did not vary with depth within the stockpiles.

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Assessment of Environmental Impacts Associated With Phosphogypsum in Florida

By Alexander May and John W. Sweeney

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ASSESSMENT OF ENVIRONMENTAL IMPACTS ASSOCIATED WITH PHOSPHOGYPSUM IN FLORIDA

By Alexander May[1] and John W. Sweeney[2]

ABSTRACT

In its role to provide technology to prevent or limit adverse environmental impacts associated with mining or minerals processing, the Bureau of Mines has conducted research at its Tuscaloosa Research Center to asess the environmental impacts of phosphogypsum produced by the Florida phosphate industry. Over the years, stockpiles containing 335 million tons of phosphogypsum have accumulated and the industry continues to generate an additional 33 million tons a year. Samples from approximately 1,000 feet of drill core, obtained from nine stockpiles were characterized using chemical, X-ray diffraction, emission spectrographic, radiological, and physical means. The data developed indicated that phosphogypsum is not a corrosive or toxic hazardous waste as defined by Environmental Protection Agency criteria. Radium concentration averaged 21 picocuries per gram and its content was inversely related to particle sizes. Thirty-nine elements were detected in phosphogypsum; concentrations of these elements did not vary with depth within the stockpiles.

INTRODUCTION

In the past 20 years there has been a constant shift in the United States toward using multinutrient and mixed fertilizers in place of single-nutrient fertilizers. This trend has brought about the localization, especially in Florida and along the gulf coast, of large raw-materials-oriented chemical companies manufacturing wet-process phosphoric acid, which is the basic material needed to produce high-analysis multinuterient fertilizers. The manufacture of wet-process phosphoric acid results in the generation of large quantities of waste gypsum. In the fertilizer industry this is usually referred to as phosphogypsum which distinguishes it from the natural gypsum mineral. As a rule, 5.5 tons of phosphogypsum are produced for each ton of phosphoric acid produced.

In 1978, U.S. production of crude natural gypsum was estimated at 14.9 million tons. Annual domestic gypsum consumption in 1978 was 24.4 million tons (10),[3] of which 700,000 tons was phosphogypsum.

By comparison, the Florida phosphate industry generates 33 million tons of phosphogypsum annually and only a small fraction (about 700,000 tons) is used for agricultural purposes. In addition, there are 334.7 million tons of the

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[3] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

material stacked on the ground in Florida. Projections indicate that by the year 2,000 over 1 billion tons of phosphogypsum will be available in Florida alone. Figure 1 shows the location of phosphogypsum stacks in Florida.

Phosphogypsum contains radium, and owing to the large tonnages in Florida, is of environmental concern. The Environmental Protection Agency (EPA) proposed in 1978 that phosphogypsum be identified as a potential hazardous waste. On May 19, 1980, EPA issued its final regulations of toxic and hazardous wastes, but as of July 1981, had deferred regulation of phosphogypsum. A part of the Bureau's Minerals Environmental Technology research program is to assess these types of problems and develop a data base so that, through a continuing research effort, potential environmental problems can be mitigated. The Bureau's Tuscaloosa Research Center conducted research to characterize phosphogypsum to determine if it is hazardous or toxic, and if so, to investigate means to mitigate the situation so that the phosphogypsum could be used in a variety of high-volume applications.

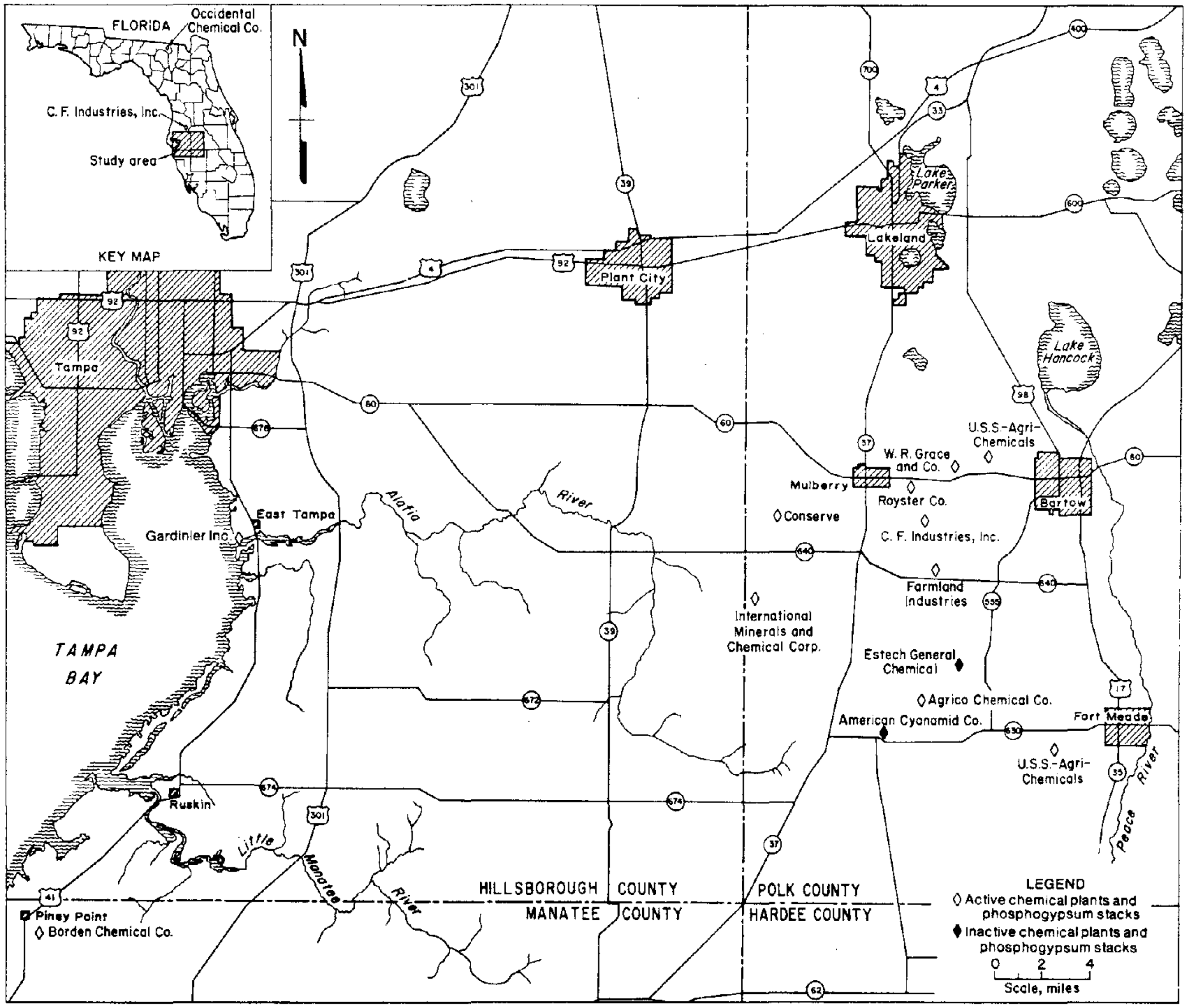

FIGURE 1. - Location of phosphogypsum stacks in Florida.

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The authors are indebted to advice and assistance in the study provided by Dr. David P. Borris, executive director, Florida Institute of Phosphate Research. The voluntary cooperation of the following Florida phosphate companies in assisting in this study is also greatfully acknowledged: Agrico Chemical Co.; American Cyanamid Co.; Borden Chemical Co.; CF Industries, Inc.; Conserve; Estech General Chemical; Farmland Industries; Gardinier, Inc.; International Minerals and Chemical Corp.; Occidental Chemical Co.; Royster Co.; U.S.S. Agri-Chemicals, and W. R. Grace and Co. Special appreciation is extended to the EPA radiation facility, Montgomery, Ala., for radiological isotope analyses.

CRITERIA FOR DEFINING HAZARDOUS WASTE

The EPA criteria defining hazardous waste were used as guidelines in this study. The EPA criterion for corrosivity is a pH equal to or less than 2 or equal to or greater than 12.5 (8). The EPA criterion for toxicity of wastes is based on an extraction procedure to identify toxic wastes likely to leach into the ground water. The hazardous nature of the waste is judged by the concentrations of specific contaminants in the extract. The contaminants listed by EPA for toxic consideration are eight metals and six chlorinated organic compounds (7). There are no probable sources of chlorinated organic compounds in the phosphogypsum or its precursor reactants. Therefore organic compounds were not investigated in this study. The Bureau of Mines considered the total concentrations of trace elements in phosphogypsum, rather than consider only the toxicity due to leachable elements. Thus, emission spectrographic analyses of the gypsum solids were used to determine trace elements, both toxic and nontoxic. These analyses were correlated with the EPA leaching tests criteria, and also provide information for the assessment of the gypsum under all conditions.

The EPA regulations, proposed December 18, 1978, for the identification of hazardous wastes listed phosphogypsum as a hazardous waste because it was radioactive. To be excluded from the list, the average radium-226 concentration would have to be less than 5 picocuries per gram of solid waste or the total quantity of radium-226 would have to be less than 10 microcuries for any single discrete source (7). The final EPA regulations, issued May 19, 1980, still list phosphogypsum as a hazardous waste but defer development of final regulation for phosphogypsum pending Congressional action (8).

PHOSPHOGYPSUM PRODUCTION

Phosphogypsum is the major byproduct of wet-process phosphoric acid production. Phosphate rock, which is composed of apatite minerals (9) (calcium phosphates containing varying amounts of carbonate and fluoride), is digested with sulfuric acid and water to produce phosphoric acid, phosphogypsum and minor quantities of hydrofluoric acid.

The reaction of the phosphate rock to produce gypsum, $CaSO_4 \cdot 2H_2O$, may be illustrated by

$$Ca_{10}(PO_4)_6F_2 + 10\ H_2SO_4 + 20\ H_2O \longrightarrow$$

$$10\ CaSO_4 \cdot 2\ H_2O + 6\ H_3PO_4 + 2HF \qquad (1)$$

Gypsum forms monoclinic crystals that are tabular and diamond-shaped. Both habits are shown in figure 2.

FIGURE 2. - Scanning electron microphotograph of phosphogypsum (X 1,000).

In the Prayon process, commonly used in Florida, the phosphate rock, ground to pass 100 mesh, is treated with 30 to 46 percent phosphoric acid and 55 to 60 percent sulfuric acid. The rock and acid is circulated through reaction tanks to maintain the optimum time and temperature for the reaction and for the growth of phosphogypsum crystals. The phosphogypsum is filtered, washed with water, and pumped as a slurry to ponds from which the phosphogypsum settles to form the phosphogypsum stacks (11).

The hemihydrate process is similar to the Prayon process but uses higher temperatures and acid concentrations in the reaction tanks. This favors the initial formulation of hemihydrate. In subsequent crystallization tanks the hemihydrate is mixed with gypsum suspensions where it recrystallizes as large crystals of the dihydrate; that is, as phosphogypsum.

Figure 3 is an aerial view of a typical phosphogypsum stack.

INVENTORY OF PHOSPHOGYPSUM

Seventeen phosphogypsum stacks were identified in Florida. Data regarding the inventory were obtained through the cooperation of the Florida Institute of

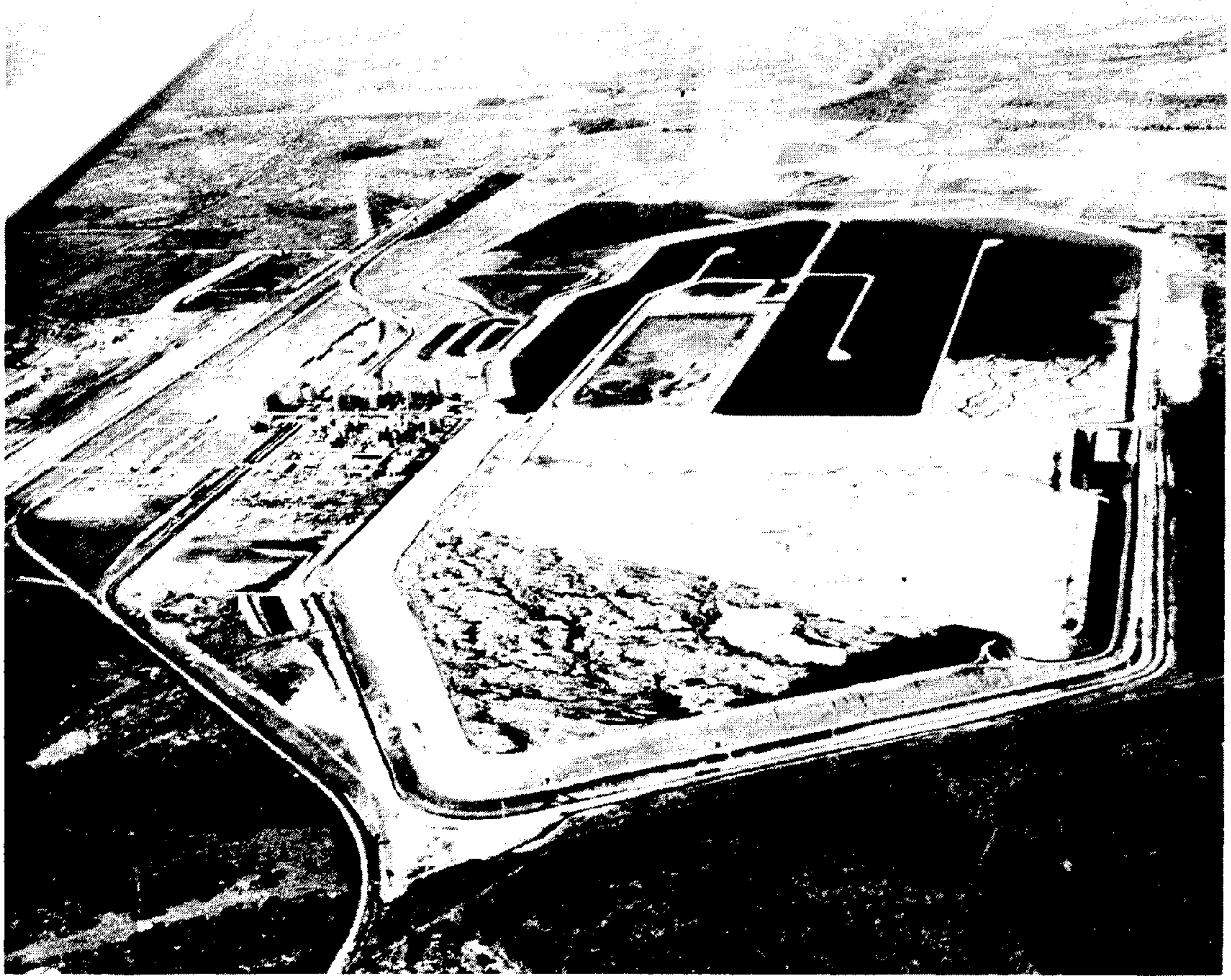

FIGURE 3. - View of a typical phosphogypsum stack in Florida.

Phosphate Research, and 13 phosphoric acid producing companies. The data shown in table 1, which were current as of April 1980, showed that 334.7 million tons of phosphogypsum have accumulated in Florida over a 16.8-year average, giving an average production rate of 19.9 million tons per year. However, the present rate of generation greatly exceeds this average (5) and is now 33.3 million tons a year. At the present rate of generation, the amount of phosphogypsum accumulated by 1985 would be 500 million tons and approximately 1 billion tons by the year 2000.

TABLE 1. - Phosphogypsum inventory

Gypsum stack identification	Year began	Year discontinued	Years in service	Acres	Annual production, thousand tons per year	Cumulative total, thousand tons
A.............	1965	Active	15	250	2,400	22,000
B.............	1947	Active	33	300	3,000	77,000
C.............	1956	1971	15	123	Inactive	18,900
D.............	1963	Active	17	340	3,700	43,080
E.............	1948	1980	32	50	Inactive	12,128
F.............	1948	1968	20	100	Inactive	5,000
G.............	1966	Active	14	284	3,500	21,304
H.............	1964	Active	15	360	1,100	16,500
I.............	1975	Active	5	300	5,500	17,361
J.............	1976	1980	4	84	Inactive	1,540
K.............	1961	Active	19	200	3,500	18,288
L.............	1954	1963	9	250	Inactive	4,000
M.............	1973	Active	7	60	1,302	5,860
N.............	1965	Active	15	400	3,016	22,709
O.............	1955	Active	25	90	750	5,830
P.............	1954	Active	26	528	4,600	32,200
Q.............	1965	Active	14	140	900	11,000
Total....			285	3,859	33,268	334,700

RATIONALE OF SAMPLING AND ANALYSES

Of the 17 phosphogypsum stacks identified, nine were sampled; these were identified as being representative of the variety of conditions encountered in either processing or storage. Of the nine sampled, six stacks were active and three were inactive. The rationale of the sampling program was to establish the uniformity and components of phosphogypsum in each stack and differences among stacks. This included differences between active and inactive stacks and between processes used in the manufacture of phosphoric acid. Of the active stacks, one produced phosphogypsum using the hemihydrate acid manufacturing process while the others produced phosphogypsum using the Prayon process. The phosphogypsum from one stack was washed in a different manner than the others prior to placing it on the stack, possibly making it atypical. The identities of the samples, letters (A through I) which represented the hemihydrate process and the different wash method were deleted to ensure company confidentiality. Of the nine stacks sampled, stack A was sampled at three locations; stacks B and C were sampled at two locations each; while each of the remaining stacks were sampled at one location.

The sampling program was designed to obtain results that would be representative of all of the phosphogypsum stacks, to show differences among stacks, and to show differences from top to bottom and across the stacks. Three types of samples were obtained.

1. Core samples.--Representative of the phosphogypsum in the entire length of a core. There were 13 core samples, one for each core drilled.

2. Interval samples.--Representative of the phosphogypsum in 10-foot-depth intervals of a core. There were 90 interval samples.

3. Sized samples.--Representative of particle size distributions of the material in the entire length of a core. There were seven sized samples.

The rationale of the analytical tests was to characterize the phosphogypsum to assess its environmental impacts. The tests included chemical analyses for major components; pH tests for acidity; emission spectrographic analyses for minor elements; radium-226, thorium, and uranium analyses for radioactivity; X-ray diffraction analyses for mineralogy; and size analyses and density determinations for physical characterization.

One chemical analysis was made of each of the 13 core samples and one X-ray diffraction analysis was made of three of the core samples to provide the major chemical and mineralogical components of the stacks.

One spectrographic, pH, and radium-226 analysis was made on each core sample, interval sample, and sized sample to provide minor elements, acidity, and radioactivity data. The analyses indicated differences among the stacks, differences from top to bottom across the stacks, and differences due to particle size distributions.

The three core samples obtained from stack A, their interval samples, and sized samples were analyzed quantitatively for trace quantities of uranium and thorium. The three core samples were also analyzed for radium, uranium, and thorium isotopes. These data were used to indicate the radioactive elements present and their relationships to each other within the stack.

Thirteen core samples were obtained from approximately 1,000 feet of phosphogypsum core. Approximately 800 analyses and tests were performed, which yielded nearly 2,400 individual data points.

TEST PROCEDURES

To establish the free water content, samples were dried at room temperature to constant weight and then at 45° C for an additional 2 hours. The dried samples were then analyzed for chemical, radiological, and trace elements. The pH measured was that of moist phosphogypsum. Water was added to phosphogypsum to produce very thick slurries into which the pH and standard electrodes were immersed and measurements taken. Except for pH and densities, the chemical and radiological results were then calculated back to the weight basis of the samples as received. The particle size distribution was determined on the dried samples. Emission spectrographic results were reported on the basis of the dried samples.

Chemical analyses were performed in accordance with American Society for Testing and Materials, Standard Methods for Chemical Analysis of Gypsum and Gypsum Products, ASTM C471-76 (1). Fluoride and phosphorus were determined by the Association of Florida Phosphate Chemists Methods (4). Uranium was determined by the fluorometric method, ASTM D2907-70T (2), and thorium by the colorimetric method, ASTM D2333-68 (3). Radium was determined by the radon emanation method (6) and uranium and thorium isotopes were determined by a chromatographic and radiological technique developed by the EPA.

TEST RESULTS

Tables 2 and 3 present the chemical analyses data. Table 4 shows the free water and table 5 shows the pH for increment samples. Table 6 gives size distribution data. Tables 7 through 10 address radium, uranium, and thorium results and table 11 lists emission spectrographic analyses.

TABLE 2. - Chemical analyses[1] of core samples of phosphogypsum, major components

Core number	Depth of core, feet	Samples as received, wt-pct					
		Free water	Combined water	SiO_2 and HCl insolubles	[2]Al_2O_3 and Fe_2O_3	[3]CaO	SO_3
A1	70	16.3	15.78	3.46	3.31	24.51	37.30
A2	70	17.2	15.55	4.92	3.48	23.69	36.92
A3	70	18.7	14.66	4.86	3.56	23.15	35.62
B1	100	14.9	13.53	5.34	4.27	22.60	35.30
B2	100	14.8	12.74	13.67	2.49	20.82	31.71
C1	50	16.7	15.24	4.76	3.29	24.44	38.31
C2	80	15.1	9.70	34.15	7.51	14.04	23.48
D	70	14.1	12.02	11.01	6.31	18.66	28.55
E	90	20.7	14.29	6.66	3.41	22.47	35.64
F	30	17.6	15.73	4.48	4.38	23.32	36.17
G	60	18.9	13.19	9.57	4.07	19.22	30.54
H	80	17.2	14.18	8.99	3.74	22.26	34.58
I	30	16.0	10.72	12.90	7.48	15.61	27.55
Average	69	16.8	13.64	9.60	4.41	21.14	33.21

[1] Analysed by ASTM C471-76, Part 5-13, Methods.

[2] Material soluble in HCl and insoluble in NH_4OH.

[3] Material soluble in HCl, soluble in NH_4OH, and insoluble in oxalate solution = CaO in phosphogypsum.

TABLE 3. - Chemical analyses of core samples of phosphogypsum, minor components

Core number	Samples as received, wt-pct			pH,[1] -log [H+]	Density, g/ml		Radium, [2]pCi/g
	NaCl	P_2O_5	F		As received	Dry at 110° C	
A1	0.01	0.67	0.49	2.30	1.57	1.08	18
A2	.01	.50	.41	2.50	1.69	1.14	17
A3	.01	.77	.40	2.55	1.63	1.12	19
B1	.03	.89	.60	2.55	1.32	1.20	20
B2	.02	.51	.64	2.65	1.40	1.22	18
C1	.01	.67	.38	2.65	1.42	1.06	20
C2	.01	2.97	.50	3.75	1.57	1.35	17
D	.01	1.85	1.05	2.85	1.49	1.31	30
E	.01	.52	.60	2.10	1.53	1.05	21
F	.01	.37	.85	3.35	1.44	1.05	38
G	.01	.32	1.81	2.70	1.56	1.19	8
H	.01	.83	.64	2.35	1.49	1.14	23
I	.01	2.48	.87	3.00	1.65	1.28	16
Average	.01	1.03	.71	2.72	1.52	1.17	20

[1] pH of moist phosphogypsum.

[2] Picocuries per gram of composite samples, as received.

TABLE 4. - Free water of 10-foot-interval samples of phosphogypsum

Depth interval, feet	Sample as received, wt-pct						
	A1	A2	A3	B1	B2	C1	C2
0- 10..................	16.0	15.8	15.7	17.5	11.0	16.1	15.5
10- 20..................	15.9	[1]14.9	[2]17.6	15.0	11.6	[1]15.8	14.2
20- 30..................	15.3	15.3	13.1	15.0	[1]10.9	16.9	13.7
30- 40..................	[2]16.4	15.0	15.3	14.9	11.3	17.0	13.2
40- 50..................	15.1	16.0	14.4	14.6	13.3	[1]18.1	[1]11.2
50- 60..................	[1]11.7	[2]16.5	16.2	14.8	12.5	NAp	13.7
60- 70..................	15.1	15.2	[1]12.6	[2]18.1	[2]15.0	NAp	21.4
70- 80..................	NAp	NAp	NAp	[1]13.2	13.8	NAp	[2]22.0
80- 90..................	NAp	NAp	NAp	15.4	11.9	NAp	NAp
90-100..................	NAp	NAp	NAp	14.4	12.7	NAp	Nap
Core average........	15.1	15.5	15.0	15.3	12.4	16.8	15.6

Depth interval, feet	Sample as received, wt-pct						Depth average, wt-pct
	D	E	F	G	H	I	
0- 10..................	12.0	[1]15.6	17.8	[1]10.8	15.9	13.0	14.8
10- 20..................	10.5	16.7	[1]17.4	12.3	14.9	[2]15.4	14.8
20- 30..................	11.6	16.5	[2]18.2	11.9	14.7	[1]11.9	14.2
30- 40..................	[1]8.5	15.8	NAp	13.7	[1]13.8	NAp	14.1
40- 50..................	12.1	15.8	NAp	11.3	14.0	NAp	14.2
50- 60..................	[2]13.5	[2]21.8	NAp	[2]14.1	14.9	NAp	15.0
60- 70..................	13.8	16.1	NAp	NAp	[2]16.9	NAp	16.0
70- 80..................	NAp	17.6	NAp	NAp	16.8	NAp	16.7
80- 90..................	NAp	17.4	NAp	NAp	NAp	NAp	14.9
90-100..................	NAp	NAp	NAp	NAp	NAp	NAp	13.6
Core average........	11.7	17.0	17.8	12.4	15.2	13.4	[3]14.8

NAp Not applicable, no sample obtained.

[1] Minimum in core.

[2] Maximum in core.

[3] Grand average, all data.

TABLE 5. - pH of 10-foot-interval samples of phosphogypsum

Depth interval, feet	Samples, pH						
	A1	A2	A3	B1	B2	C1	C2
0- 10	2.15	2.45	2.45	2.85	3.25	4.35	3.80
10- 20	2.15	2.35	2.45	2.80	3.40	3.85	3.60
20- 30	2.25	2.40	2.50	2.95	3.15	2.80	3.85
30- 40	2.10	2.40	2.50	2.60	3.05	2.60	3.40
40- 50	2.20	2.40	2.35	2.80	3.05	2.60	3.65
50- 60	2.20	2.50	2.40	2.75	3.05	NAp	4.40
60- 70	2.25	2.55	2.50	2.80	2.95	NAp	5.15
70- 80	NAp	NAp	NAp	2.70	2.95	NAp	5.50
80- 90	NAp	NAp	NAp	2.80	3.10	NAp	NAp
90-100	NAp	NAp	NAp	3.00	3.20	NAp	NAp
Core average	2.19	2.44	2.45	2.80	3.11	3.24	4.17
Depth interval, feet	Samples, pH						Depth average, pH
	D	E	F	G	H	I	
0- 10	2.85	2.55	3.70	2.80	2.65	2.75	2.97
10- 20	2.75	2.40	3.75	2.90	2.60	2.40	2.88
20- 30	2.80	2.40	3.50	2.90	2.40	2.65	2.81
30- 40	2.45	2.60	NAp	2.35	2.60	NAp	2.60
40- 50	2.55	2.60	NAp	2.70	2.50	NAp	2.67
50- 60	2.50	2.60	NAp	2.50	2.65	NAp	2.75
60- 70	2.60	2.40	NAp	NAp	3.20	NAp	2.93
70- 80	NAp	2.40	NAp	NAp	4.00	NAp	3.51
80- 90	NAp	2.50	NAp	NAp	NAp	NAp	2.80
90-100	NAp	NAp	NAp	NAp	NAp	NAp	3.10
Core average	2.64	2.49	3.65	2.69	2.82	2.60	[1]2.85

NAp Not applicable, no sample obtained.

[1] Grand average, all data.

TABLE 6. - Particle size distribution of sized samples of phosphogypsum[1]

Sieve opening, mm	Sample						
	A1	A2	A3	B1	B2	C2	G
Coarse:							
Plus 0.710	4.6	10.4	6.6	2.0	1.9	7.2	4.6
Minus 0.710 plus 0.500	3.6	9.1	5.3	4.6	5.1	7.5	4.5
Minus 0.500 plus 0.250	6.4	12.0	9.1	15.1	35.8	20.1	11.9
Total	14.6	31.5	21.0	21.7	42.8	34.8	21.0
Medium:							
Minus 0.250 plus 0.180	3.6	4.2	5.0	11.9	27.6	8.3	7.8
Minus 0.180 plus 0.125	4.9	9.8	6.3	13.0	12.9	25.5	8.9
Minus 0.125 plus 0.063	15.6	11.8	15.6	24.2	11.5	12.5	24.9
Minus 0.063 plus 0.045	12.0	13.1	13.9	11.0	3.0	8.0	6.7
Total	36.1	38.9	40.8	60.1	55.0	54.3	48.3
Fine: Minus 0.045	49.3	29.6	38.2	18.2	2.2	10.9	30.7
Cumulative:							
Plus 0.710	4.6	10.4	6.6	2.0	1.9	7.2	4.6
Plus 0.500	8.2	19.5	11.9	6.6	7.0	14.7	9.1
Plus 0.250	14.6	31.5	21.0	21.7	42.8	34.8	21.0
Plus 0.180	18.2	35.7	26.0	33.6	70.4	43.1	28.8
Plus 0.125	23.1	45.5	32.3	46.6	83.3	68.8	37.7
Plus 0.063	38.7	57.3	47.9	70.8	94.8	81.1	62.6
Plus 0.045	50.7	70.4	61.8	81.8	97.8	89.1	69.3

[1] Dried to constant weight at 45° C.

TABLE 7. - Uranium, thorium, and radium analyses of sized as-received samples of phosphogypsum

(Picocuries per gram)

Core number and size of sample	[1]U	[2]Th	[3]Ra
Core A1:			
Coarse[4].............	4.3	NA	23
Medium[5].............	3.4	NA	21
Fine[6]...............	4.3	3.8	27
Average[7]..........	4.0	NA	24
Core A2:			
Coarse...............	8.4	NA	19
Medium...............	3.6	NA	22
Fine.................	3.4	NA	30
Average...........	5.0	NA	23
Core A3:			
Coarse...............	4.4	3.7	23
Medium...............	4.7	NA	15
Fine.................	6.1	NA	24
Average...........	5.2	NA	20
Core B1:			
Coarse...............	5.8	3.9	20
Medium...............	8.7	11.6	26
Fine.................	5.8	3.9	26
Average...........	7.5	8.5	25
Core B2:			
Coarse...............	9.5	3.9	15
Medium...............	6.0	3.9	21
Fine.................	6.0	NA	22
Average...........	7.5	NA	18
Core C2:			
Coarse...............	5.4	27.0	21
Medium...............	20.7	7.7	16
Fine.................	9.5	NA	30
Average...........	14.2	NA	19
Core G:			
Coarse...............	4.7	14.7	8.9
Medium...............	2.5	25.8	6.7
Fine.................	2.5	7.4	10.5
Average...........	3.0	17.8	8.3

NA Not available.

[1] Analyses by ASTM D2907-70T fluorometric method.

[2] Analyses by ASTM D2333-68 colorimetric method.

[3] Analyses by radon emanation method.

[4] Plus 0.250 mm.

[5] Minus 0.250 plus 0.045 mm.

[6] Minus 0.045 mm.

[7] Averages are weighted based on amount in each fraction, in percent, and the amount of the elements in each sample, in picocuries per gram.

TABLE 8. - Radiological isotopic analyses of as-received core samples of phosphogypsum

(Picocuries per gram)

Isotope	Core		
	A1	A2	A3
Radium.................	16.10	13.50	13.30
Uranium-234............	2.14	1.47	2.44
Uranium-235............	.17	.13	.15
Uranium-238............	2.13	1.61	2.41
Thorium-227............	.61	.47	.59
Thorium-228............	.03	.03	.06
Thorium-230............	3.30	1.95	3.91
Thorium-232............	.13	.07	.11

TABLE 9. - Radium analyses of 10-foot-interval as-received samples of phosphogypsum

(Picocuries per gram)

Depth interval, feet	Sample						
	A1	A2	A3	B1	B2	C1	C2
0- 10................	19	26	28	13	20	19	21
10- 20................	25	26	21	18	16	24	26
20- 30................	23	27	18	15	17	20	20
30- 40................	18	19	17	20	20	22	18
40- 50................	23	18	16	15	16	25	10
50- 60................	19	24	18	19	18	NAp	12
60- 70................	18	24	16	24	16	NAp	17
70- 80................	NAp	NAp	NAp	14	21	NAp	[1] 0.9
80- 90................	NAp	NAp	NAp	25	19	NAp	NAp
90-100................	NAp	NAp	NAp	24	24	NAp	NAp
Core average	20.7	23.4	19.1	18.7	18.7	22.0	17.7

Depth interval, feet	Sample						Depth average
	D	-E	F	G	H	I	
0- 10................	22	18	37	8.9	17	24	21.0
10- 20................	24	20	45	8.8	20	30	23.4
20- 30................	34	24	44	9.7	16	23	22.4
30- 40................	22	21	NAp	11.2	24	NAp	19.3
40- 50................	34	26	NAp	8.9	27	NAp	19.9
50- 60................	26	20	NAp	10.3	26	NAp	19.2
60- 70................	33	24	NAp	NAp	24	NAp	21.8
70- 80................	NAp	21	NAp	NAp	11	NAp	16.8
80- 90................	NAp	15	NAp	NAp	NAp	NAp	19.7
90-100................	NAp	NAp	NAp	NAp	NAp	NAp	24.0
Core average.....	27.9	21.0	42.0	9.6	20.6	25.7	[2]20.91

NAp Not applicable, no sample obtained.

[1] Not included in averages.

[2] Grand average, all data.

TABLE 10. - Uranium and thorium analyses of 10-foot-interval as-received samples of phosphogypsum

(Picocuries per gram)

Depth interval, feet	Sample								Depth average	
	A1		A2		A3		G		U	Th
	U	Th	U	Th	U	Th	U	Th		
20-30...............	4.0	NA	3.1	NA	4.1	3.7	2.4	14.7	3.4	NA
30-40...............	4.0	NA	2.9	NA	3.7	NA	3.2	14.7	3.5	NA
40-50...............	3.7	3.8	3.1	3.7	5.0	3.7	3.9	25.8	3.9	9.2
50-60...............	4.8	NA	3.1	NA	5.1	3.7	2.3	18.4	3.8	NA
60-70...............	4.3	NA	3.1	NA	5.9	7.4	NAp	NAp	4.4	NA
Core average...	4.2	NA	3.1	NA	4.8	NA	3.0	18.4	3.8	NA

NA Not available because thorium was detected in amounts too small for quantitative results.

NAp Not applicable, no sample obtained.

TABLE 11. - Emission spectrographic analyses of phosphogypsum

Element detected	Average,[1] ppm	Number detected in	
		Cores	Samples
Aluminum	1,360	13	110
Antimony	111	2	10
Arsenic	42	7	37
Barium	7	2	8
Bismuth	1	2	6
Boron	3	8	37
Beryllium	1	1	1
Cadmium	7	1	1
Cobalt	2	7	33
Copper	8	13	106
Iron	670	13	110
Lead	1	6	6
Magnesium	1,220	13	110
Manganese	15	13	72
Molybdenum	16	3	13
Nickel	2	11	57
Platinum	<1	2	5
Potassium	11	9	56
Rhenium	11	6	23
Silver	<1	4	6
Sodium	252	13	91
Strontium	10	11	79
Tantalum	2	2	5
Tin	4	5	13
Titanium	4,020	13	110
Tungsten	29	3	9
Vanadium	19	13	110
Yttrium	2	3	9
Zinc	9	10	50
Zirconium	10	8	12

[1] Average in cores in which element detected, from analyses of core samples, sized samples, and interval samples.

The X-ray diffraction analyses were performed on core samples A1, B1, and F. All gave the same results. Only gypsum and alpha-quartz were detected. The limit of detection was about 5 percent of a mineral present. Fluorides and phosphates were present, as well as compounds of aluminum, magnesium, iron, and other elements. However, these compounds were present at less than 5 percent and were not detected by the X-ray diffraction.

DISCUSSION

The chemical analyses given in tables 2 and 3 lists quantities of the major components of phosphogypsum. The analyses in table 2 and that of sodium chloride in table 3 were performed by the Standard Methods for Chemical Analysis of Gypsum anf Gypsum Products (1). Although standard analytical methods were used, phosphogypsum differes sufficiently from gypsum to require scrutiny of the results. In the standard gypsum analysis, iron and aluminum are determined by removing silicon and acid-insoluble material and then precipitating the iron and aluminum as hydroxides. The hydroxides are ignited to form oxides and the iron and aluminum oxides are then weighed. However, phosphogypsum contains phosphates and fluorides which accompany iron and aluminum hydroxides in their analytical determination. These precipitate as calcium phosphates and calcium fluorides. Titanium oxide may also contaminate the iron and aluminum hydroxides. The results for "iron and aluminum oxides," as designated in reference 1 were thus higher than the actual quantity of iron and aluminum oxides present. Calcium content is determined in the filtrate remaining after removing the silicon, acid-insoluble material, iron, aluminum, and calcium phosphates and fluorides. The calcium content determined in this manner represented that which was present in the phosphogypsum. The other analyses were not affected.

A typical phosphogypsum composition is shown in table 12. The results in table 12 are from the analyses of the core samples, excluding samples C2, D, and I. The core for sample C2 was taken from part of a phosphogypsum stack that had been placed in a phosphate rock mined-out area. The base of phosphate mine pits are uneven in elevation and contain overburden spoil. The unusual results for sample C2 were checked with three different composite samples. Also, the C2 interval samples from 10 to 20 feet and from 70 to 80 feet were analyzed petrographically. These analyses showed that the greater depth had high silica and low gypsum and at shallower depth content was reversed. Results for C2, namely high silica, iron, aluminum, phosphorus, uranium, and pH, and low calcium, sulfur, and combined water, plus petrographic analyses; indicated that the core penetrated overburden spoil. Sample D was from a stack placed below ground level and sample I from a new stack. The analytical evidence indicates C2, D, and I results were not completely typical of phosphogypsum due to possible contamination by overburden at the gypsum-ground interface.

TABLE 12. - Typical composition of phosphogypsum from Florida[1]

Component	Average	Low	High
Composition of sample, as received, wt-pct:			
Moisture	17.30	14.8	20.7
Combined water	14.49	12.7	15.8
Silicon dioxide and acid insoluble	6.67	3.5	9.6
Acid soluble, NH_4OH insoluble	3.60	3.3	4.4
Calcium oxide	22.65	19.2	24.5
Sulfur trioxide	35.21	30.5	38.3
Sodium chloride	.01	.01	.03
Sum	99.93	NAp	NAp
HCl soluble, NH_4OH, insoluble fraction, wt-pct:			
Phosphorus pentoxide	0.61	0.32	0.83
Fluorine	.68	.38	1.81
Aluminum oxide[2]	.29	.00	.50
Ferric oxide[2]	.10	.00	1.00
Titanium dioxide[2]	.63	.00	1.00
Calcium oxide equivalent of P_2O_5 and F[3]	1.24	.69	3.00
Sum	3.55	1.39	8.14
Density...g/ml	1.51	1.32	1.69
pH	2.57	2.10	3.35
Radium...pCi/g	20.2	8.00	38.00
Gypsum...wt-pct	69.23	60.67	75.48

NAp Not applicable.

[1] Calculated quantities from data for sample A1, A2, A3, B1, B2, C1, E, F, G, and H.

[2] Aluminum, iron, and titanium analyses from emission spectrographic results.

[3] As calcium dihydrogen phosphate and calcium fluoride.

[4] Calculated from percent combined water. For the average, this gives 0.10 percent calcium oxide and 3.02 percent sulfur trioxide not in gypsum.

The bulk densities shown in table 3 indicated that so significant difference existed among the stacks in compaction of the phosphogypsum. The pH and radium results in table 3 are those of the core samples. Discussion of pH and radium follows in conjunction with tables 5 and 9.

Free water, shown in table 4, represented moisture not bound as water of crystallization. No pattern for the seepage of water through the stacks was apparent from the data. The maximum free water content for each core occured at depth intervals from 10 to 80 feet, but also the minimum occurred at depth intervals from 0 to 80 feet. The wettest and driest depth intervals even occurred adjacent to each other. For example, in core B1, the 60- to 70-foot interval was the wettest and the 70- 80-foot interval the driest. In core B1 the first sample was like mud, the second like rock. Analysis of variance (ANOVA) of the data showed that there was no significant difference in free water among depths and there was a significant difference among cores.

The pH values, shown in table 5, were all greater than 2.0 and less than 12.5. Every individual pH measurement on all 10-foot-interval samples and the core samples given in table 3 were also greater than 2.0 and less than 12.5. This is significant because EPA defined a hazardous waste by the criterion of corrosivity as one that had a pH equal to or less than 2 or equal to or greater than 12.5. Therefore, all phosphogypsum samples obtained in this investigation were not hazardous wastes by the EPA criterion of corrosivity.

Analysis of variance of the pH data showed that differences among cores and among depths were significant. This was also found when the atypical samples C2, D, and I were excluded. However, when ANOVA was applied to A1, A2, A3 and also separately to B1 and B2, no significant difference was found in pH with depth or with cores. The highest pH values were for samples C1, C2, and F. All of these are from inactive stacks; the C stack had been inactive 9 years and the F stack 12 years. The pH values, 4.40, 5.15, and 5.50 for C2 may be due to this core penetrating overburden spoil, as previously mentioned. Excluding these high C2 pH values, the remaining pH values for C2 average 3.66 which is still the highest pH value of the cores. The higher pH values for these inactive stacks indicate rainwater may leach hydrogen ion and thus lower the acidity of the stacks.

Particle size distribution is shown in table 6. Three size distributions were used for uranium, thorium, radium, and emission spectrographic analyses. These were the total coarse size (retained on 0.25-mm sieve), total medium size (passes 0.25-mm sieve, retained on 0.045-mm sieve) and fine size (passes 0.045-mm sieve). The coarse, medium, and fine fractions are also convenient summaries of the data. The cumulative percent distribution is a linear function of the logarithm of the sieve opening.

Uranium, thorium, and radium analyses of sized samples are shown in table 7. The uranium and thorium analyses were for total uranium and total thorium and the original data were measured in parts per million. The parts-per-million uranium was multiplied by 0.6781 and the parts-per-million thorium by 4.5423 to convert them to picocuries per gram, for comparison to radium data. The factors used in the conversions were based on assuming the natural isotopic abundance of uranium and thorium isotopes. About one-half of the thorium data were reported as "less than 1 ppm." Since these data could not be accurately analyzed, they were included in tables 7 and 10 as not available.

The average concentrations of uranium and radium for the coarse, medium, and fine fractions are shown in table 13. Radium was most concentrated in the fine fraction and ANOVA verified that a significant difference existed among the sizes. The results in table 13 also indicate differences in uranium concentrations with size functions. However, ANOVA indicates these differences are not significant. Insufficient data were available to statistically analyze thorium data.

TABLE 13. - Average uranium and radium contents of sized as-received samples of phosphogypsum

(Picocuries per gram)

Size	Samples	
	U	Ra
[1]Coarse......................	6	19
[2]Medium......................	7	18
[3]Fine......................	5	24

[1]Plus 0.250 mm.
[2]Minus 0.250 plus 0.045 mm.
[3]Minus 0.045 mm.

Table 8 shows the isotopic analyses of radium, uranium, and thorium in three samples. These results indicated that uranium-238, uranium-234, and thorium-230 were about in equilibrium. Radium was not in equilibrium and was more concentrated in the phosphogypsum than the radiological equilibrium with thorium-230 would allow.

Table 9 shows the analyses of the 10-foot-interval samples for radium. The average of these data and comparison with the composite samples average are shown in table 14.

TABLE 14. -Average radium concentrations of as-received phosphogypsum samples

(Picocuries per gram)

Samples	Average
Composite	20.4
10-foot interval	20.9
Composite (excluding C2, D, and I)	20.2
10-foot interval (excluding C2, D, and I)	20.3
All data: Core, 10-foot interval, and sized	20.5

The EPA proposed regulations of December 18, 1978, stated that 5 pCi Ra/g or greater would cause a waste to be a hazardous waste because of radioactivity (7). However, on May 19, 1980, EPA deferred radiation limits on phosphogypsum (8), so at this time it cannot be stated that the phosphogypsum was a radiation hazard based on EPA criteria.

Sample G was low in radium compared to the other phosphogypsum stacks. This low content occurred because the phosphate rock that produced the phosphogypsum in stack G contained about one-third the uranium and radium that the phosphate rock that produced the phosphogypsum in the other stacks contained. Sample F is higher in radium than the other samples. It is not known at this time why this occurs.

ANOVA calculations were performed on the data in table 9. Using all of the data, the ANOVA showed, among cores, a significant difference in radium content at the 99-percent-confidence level, and showed that the difference in radium content was not significant with depth. The same was found when samples C2, D, and I were excluded. When samples A1, A2, and A3 were examined no significant differences were indicated among samples or among depths. The same was true with samples B1 and B2. This statistical analysis indicated that radium is uniformly distributed in each stack.

Table 10 shows uranium and thorium analyses of 10-foot interval samples. Analysis of the data indicated that uranium is also uniformly distributed in each stack. Thorium data were insufficient for an accurate statistical analysis.

Emission spectrographic analyses were performed on 13 core samples, on 90 10-foot-interval samples and on 7 sized samples. This yielded 1,780 individual analytical results for semiquantitative concentrations of 30 elements. These results are summarized in table 11.

The averages shown in table 11 are the sums of all concentrations detected for a given element divided by the total number of analyses of the cores in which the element was detected. Thus the data summarizes concentrations only in cores in which elements were detected. For example, 57 analyses of nickel in 11 cores gave an average concentration of 2 ppm. Two cores contained no nickel but these zero values were not included in calculating the 2-ppm average.

In addition to the emission spectrographic data summary in table 11, the concentrations of each of 30 elements were tabulated by core versus depth. These tables are not included in this report because of the quantity of data. The emission spectrographic data, so tabulated, were statistically analyzed for 23 of the 30 elements listed in table 11 by ANOVA at the 99-percent-confidence level. The seven elements not analyzed by ANOVA were detected in less than eight samples and their data precluded the use of analysis of variance.

In every case the ANOVA indicated that there was no significant differences in concentrations of the elements with depth. Eleven elements, aluminum, arsenic, iron, magnesium, molybdenum, potassium, sodium, tin, titanium, tungsten, and vanadium showed a significant difference in concentrations among cores. The other 12 elements showed no significant difference in concentrations among cores. When considering a single phosphogypsum stack, B, and the 11 elements that showed a significant difference among cores, the ANOVA indicated no difference in concentrations with depth or between cores B1 and B2.

These results indicated that trace elements were uniformly distributed in the phosphogypsum stacks. A uniform distribution of trace elements in the stacks would occur if the same quantities of trace elements were added to the stacks as were removed through leaching. However, three stacks, C, E and F are inactive. Stack C has been idle 9 years, stack E has been idle several months, and stack F has been idle 12 years. In spite of about 40 inches of rainfall a year (12 P. IV) for 9 and 12 years, stacks C and F also showed no significant difference in concentrations of trace elements with depth. Thus, the results indicated that trace elements were not only uniformly distributed in the stacks, but are not leached from the stacks in any significant amount. This also applied to sodium, potassium, copper, and nickel whose sulfates are soluble.

The elements, arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver are listed as contaminants for characteristics of toxicity by EPA (8). Chromium, mercury, and selenium were not detected in the phosphogypsum. The detection limits for direct-current arc emission spectrographic analysis are 0.001 percent for chromium, 0.05 percent for mercury, and 0.10 percent for selenium. Barium, cadmium, lead, and silver were detected at concentrations far less than allowable by EPA requirements, even assuming that 100 percent of these elements would be extracted by the EPA procedure. The average arsenic concentration was also less than allowable by EPA requirements. However, two cores, F and H, contained 124 and 113 ppm arsenic, respectively. If 100 percent of the arsenic present were extracted by the EPA extraction procedure (8), the extracts from these cores would contain 6.20 and 5.65 ppm arsenic which exceeds the EPA allowable concentration of 5.0 ppm arsenic. However, the analysis of the data indicated that the trace elements would not be leached from the phosphogypsum. Therefore, the phosphogypsum would not be a toxic hazardous waste. Further work is in progress to perform the EPA extraction procedure and confirm this conclusion. The results will be reported in a subsequent publication.

CONCLUSIONS

Based on the research conducted at the Bureau's Tuscaloosa Research Center, phosphogypsum was generated at a rate of 33 million tons a year in Florida. The amount of accumulated phosphogypsum in Florida was 335 millions tons, and this quantity is projected to reach over 1 billion tons by the year 2000.

Phosphogypsum was not a corrosive hazardous waste. Its pH was greater than 2.0.

The radium concentration in phosphogypsum in Florida averaged 21 picocuries per gram and its concentration was greatest in the fine sizes.

Thirty-nine elements were detected in phosphogypsum; 30 by emission spectrography, three radiologically, and six by chemical analyses.

The concentrations of elements listed by EPA for toxic elements each average less than the allowable toxic elements criteria for toxic hazardous waste.

The concentrations of elements in phosphogypsum stacks did not vary with depth.

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