RI 8776

Bureau of Mines Report of Investigations/1983

Evaluation of Radium and Toxic Element Leaching Characteristics of Florida Phosphogypsum Stockpiles

By Alexander May and John W. Sweeney

UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 8776

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MARCH 3, 1849

UNITED STATES DEPARTMENT OF THE INTERIOR
James G. Watt, Secretary

BUREAU OF MINES
Robert C. Horton, Director

Research at the Tuscaloosa Research Center is carried out under a memorandum of agreement between the Bureau of Mines, U.S. Department of the Interior, and the University of Alabama.

This publication has been cataloged as follows:

May, Alexander

Evaluation of radium and toxic element leaching characteristics of Florida phosphogypsum stockpiles.

(Report of investigations / Bureau of Mines ; 8776)

Bibliography: p. 17-18.

Supt. of Docs. no.: I 28.23:8776.

1. Phosphogypsum—Environmental aspects—Florida. 2. Leaching. 3. Radium—Analysis. I. Sweeney, John W. II. Title. III. Series: Report of investigations (United States. Bureau of Mines ; 8776)

TN23.U43 [TD196.P46] 622s [661'.43] 83-600072

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

ft	foot	mL	milliliter
g	gram	µg	microgram
hr	hour	pCi	picocurie
in	inch	pct	percent by weight
L	liter	s	second
mg	milligram	wk	week
min	minute	yr	year

EVALUATION OF RADIUM AND TOXIC ELEMENT LEACHING CHARACTERISTICS OF FLORIDA PHOSPHOGYPSUM STOCKPILES

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

ABSTRACT

The Bureau of Mines conducted studies to determine if phosphogypsum, a waste material from the processing of phosphate rock, contains hazardous toxic materials as defined by the Environmental Protection Agency (EPA) and whether leaching of these toxic materials and radium may occur.

Samples of the phosphogypsum stockpiled material were evaluated using the EPA extraction procedure, atomic absorption, neutron activation, X-ray diffraction, and chemical and physical means. Radiological tests performed used both the germanium-lithium and emanation methods.

The data show that the phosphogypsum stockpiles are not hazardous toxic waste as defined by EPA criteria. Trace elements and radium are not leached from the phosphogypsum stockpiles. Absorption of trace elements and radium by phosphogypsum is the major reason for their not being leached. The standard error of measurement of radium concentrations was 4.7 pCi/g.

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INTRODUCTION

The Bureau of Mines has completed a 2-yr research study assessing potential environmental effects associated with phosphogypsum in Florida. Phosphogypsum and gypsum are both calcium sulfate dihydrate. The name "phosphogypsum" is used to designate the byproduct of phosphoric acid production, while "gypsum" refers to the natural mineral. The first phase (7)[3] of the study developed baseline data to assess whether there were any environmental problems associated with the storage of phosphogypsum. The second phase, the subject of this report, evaluated the leaching characteristics of the phosphogypsum stockpiles.

The phosphate industry in Florida is a vital segment of the Nation's economy and provides a critical mineral required for fertilizer production. In 1981, Florida and North Carolina supplied 86 pct of the domestic and 33 pct of the world's phosphate requirement (11). About 82 pct of the phosphate is converted into phosphoric acid, which is used to make fertilizers.

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

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

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

In the Prayon process, commonly used in Florida, the phosphate rock, ground to pass 100 mesh, is treated with 30 to 46 pct phosphoric acid and 55 to 60 pct sulfuric acid. The rock and acid are 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.

The hemihydrate process is similar but uses higher temperatures and acid concentrations in the reaction tanks. This favors the initial formation 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 (7).

By 1980 about 335 million tons of phosphogypsum had accumulated in Florida in 17 phosphogypsum stockpiles or stacks (fig. 1). These piles occupied an average area of 227 acres each and ranged from 30 to 140 ft in height. Additional phosphogypsum is being generated at a rate of about 33 million tons per year, and the projected accumulation by the year 2000 will be over a billion tons (7).

The first phase of the Bureau's research (7) showed that phosphogypsum was not corrosive by EPA criteria. The study also presented evidence that phosphogypsum would not be toxic by EPA criteria and that trace elements and radium would not be leached from the stockpiles. These conclusions were obtained from statistical analyses of extensive quantities of spectrographic and radiological data. More direct confirmation of these conclusions was needed to decisively answer the question of leaching of toxic elements and radium from phosphogypsum stockpiles.

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

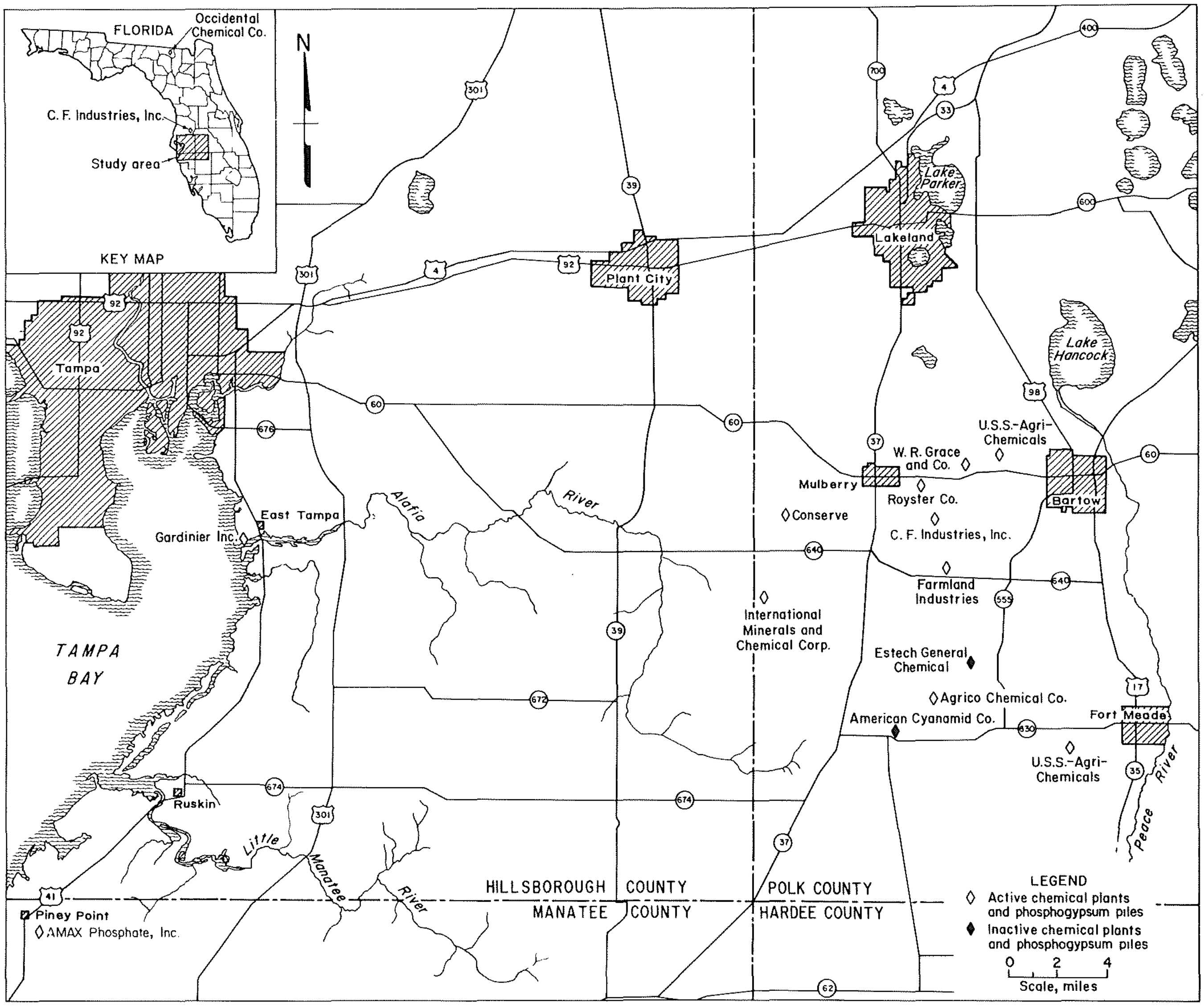

FIGURE 1. - Location of phosphogypsum piles in Florida.

This investigation took a direct approach--that is, sampling and analyzing phosphogypsum at the bottom of the stockpiles and the underlying materials in the subsurface--to determine if leaching had occurred. In addition, the standard EPA extraction procedure was performed.

ACKNOWLEDGMENTS

The authors wish to acknowledge the assistance of Dr. David P. Borris, Executive Director, Florida Institute of Phosphate Research (FIPR), for his advice and cooperation in the study under a Memorandum of Agreement between the Bureau of Mines and FIPR. The voluntary cooperation of the following Florida phosphate companies in assisting in this study is also gratefully acknowledged: Agrico Chemical Co., Estech General Chemical, Farmland Industries, Gardinier, Inc., and U.S.S. Agri-Chemical. Special appreciation is extended to the EPA radiation facility, Montgomery, AL, and the Oak Ridge National Laboratory, Oak Ridge, TN, for radium analyses.

SAMPLES

Thirteen core samples were used from the earlier study of the environmental impact of phosphogypsum production (7). The sample identifications are the same as in that work: A through I each represents an individual stockpile, and 1, 2, and 3 represent different cores on the same stockpile. Five additional core samples were obtained for this study. The new samples were taken only through a short section approximately 10 ft above and 10 ft below the interface with the ground surface. The samples contained phosphogypsum or soil. The sample identifications are the same as before: A, B, F, and H refer to the same stockpile as in reference 7; 1 and 2 refer to different cores on the same stockpile, but the samples are differentiated from the former samples by "-2," for example, F2-2. All sample depths are measured from the tops of the stockpiles of phosphogypsum.

In obtaining these five cores, the positions of the interfaces were determined by test holes. Then the drilling rig was moved about 20 ft from the test holes to drill for the samples. In addition to depending on the position of the interfaces, chemical analyses were employed to verify the nature of the samples.

TEST PROCEDURES

The leachabilities of toxic hazardous material were determined using the EPA extraction procedures (1). The leachabilities of certain metals (Cu, Ni, K, and Na) that are not considered toxic were also determined. Samples were stirred 24 hr in water and filtered; then the water-soluble concentrations were determined by atomic absorption. These metals form highly soluble sulfates that would be very susceptible to leaching and provide a test of the degree of ease of leaching within the phosphogypsum stacks.

Total concentrations of trace elements were determined by neutron activation analyses and atomic absorption. Radium concentrations were determined by the emanation method and by the germanium-lithium counting of natural radioactivity, corrected by reference to a National Bureau of Standards uranium ore. Chemical analyses were performed by standard methods.

The permeablity of phosphogypsum was also determined to help understand the effect of rainwater on leaching of trace elements. The standard variable-head method was modified in the following manner. One hundred grams of phosphogypsum was placed, as a slurry, in a glass tube 22.2 in long and 0.71 in. in internal diameter. After settling and being compacted with a rod, the phosphogypsum column was 8.37 in long with a density of 1.85 g/mL. A column of this density could support a weight equivalent to a water head of 51 ft, which approximated the conditions within phosphogypsum stockpiles. Water was placed in the tube, and as the water seeped through the column of phosphogypsum, the water levels and time intervals were recorded.

Since the solubility of gypsum is only 0.2 pct, any rainwater seeping through a phosphogypsum stockpile would be saturated with gypsum. Leaching of trace elements, thus, would be due to a saturated gypsum solution, not to water alone. An X-ray diffraction analysis was performed to determine the trace elements present in saturated aqueous solutions of phosphogypsum. One thousand grams of phosphogypsum were stirred with 2,000 mL of distilled deionized water for 24 hr. The water was filtered and allowed to evaporate at room temperature. The crystals formed by evaporation were washed with water, air-dried again, and then dried a few minutes at 60° C before being analyzed by X-ray diffraction.

Neutron activation analyses were performed at the Oak Ridge National Laboratories, for both short- and long-half-life radionuclides, using irradiation times of 20 sec and 30 min and counting times of 15 to 20 min, 1 day, 4 days, and 3 wk.

TEST RESULTS

EPA EXTRACTION PROCEDURE

The EPA criteria defining hazardous and toxic waste were used as guidelines in this study. 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 (1).

Table 1 lists the EPA contaminants and the criteria that EPA has established to constitute a hazardous toxic waste. Table 2 shows the concentrations of the inorganic contaminants in the extract from the phosphogypsum samples. All of the organic compounds listed by EPA as hazardous toxic wastes were tested by the standard EPA procedure; none were detected. These included Endrin, Lindane, Methoxychlor, toxaphene, 2,4-D, and 2,4, 5-TP Silvex. All of the metals listed in table 1 were found to be present in the extract at concentrations lower than allowed by EPA, as shown in table 2. Therefore, by EPA definition phosphogypsum is not a hazardous toxic waste material. This confirms earlier research conclusions (7) that the leaching of trace elements from phosphogypsum is not significant in introducing hazardous toxic waste materials into the environment.

TABLE 1. - Maximum concentrations of contaminants for characteristics of EPA toxicity[1]

Contaminant	Maximum concentration,[2] mg/L
Arsenic	5.0
Barium	100.0
Cadmium	1.0
Chromium	5.0
Lead	5.0
Mercury	.2
Selenium	1.0
Silver	5.0
Endrin (1,2,3,4,10,10-hexachloro-1,7-epoxy-1,4,4a,5, 6,7,8,8a-octahydro-1,4-endo, endo-5,8-dimethano naphthalene)	.02
Lindane (1,2,3,4,5,6-hexachlorocyclohexane, gamma isomer)	.4
Mathoxychlor (1,1,1-trichloro-2,2-bis [p-methoxyphenyl] ethane)	10.0
Toxaphene ($C_{10}H_{10}Cl_8$, technical chlorinated camphene, 67-69 pct Cl)	.5
2,4-D (2,4-dichlorophenoxyacetic acid	10.0
2,4,5-TP Silvex (2,4,5-trichlorophenoxypropionic acid)	1.0

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[1] From Federal Register (1).

[2] Maximum allowable concentrations in extract.

TABLE 2. - Concentrations of toxic elements in extract from EPA extraction procedure[1]

Sample	Toxic element, mg/L							
	As	Ba	Cd	Cr	Pb	Hg	Se	Ag
AL...........	0.020	0.2	0.01	0.04	0.01	0.000	0.002	0.08
A2...........	.019	.2	.01	.05	.03	.000	.003	.07
A3...........	.029	.0	.02	.06	.00	.000	.005	.10
B1...........	.014	.0	.01	.07	.01	.000	.004	.01
B2...........	.011	.2	.01	.01	.00	.001	.003	.04
C1...........	.016	.2	.02	.02	.00	.001	.005	.04
C2...........	.007	.4	.03	.05	.00	.001	.003	.10
D............	.009	.0	.01	.11	.01	.001	.003	.09
E............	.005	.2	.03	.03	.03	.001	.004	.06
F............	.002	.1	.01	.01	.04	.001	.002	.05
G............	.005	.3	.01	.01	.01	.001	.002	.08
H............	.018	.3	.01	.05	.00	.001	.003	.04
I............	.019	.2	.01	.02	.01	.004	.002	.07
Avg.....	.013	.2	.01	.04	.01	.001	.003	.06

[1] From Federal Register (1).

PHOSPHOGYPSUM-SUBSURFACE MATERIAL

Major Components

Five phosphogypsum-subsurface samples were obtained from cores by drilling through approximately the bottom 10 ft of the phosphogypsum stacks and the top 10 ft of the underlying subsurface soils. Chemical analyses were used to identify the nature of the samples and confirm that subsurface levels had been reached. The results of chemical analyses for the major components of the five samples are given in table 3. The approximate mineral compositions of the samples are shown in table 4. The approximate mineral compositions of the samples were derived from the chemical compositions by calculating the amount of gypsum, sand and clay, and phosphate rock present.[4]

As shown in table 3, the moisture content of subsurface material under the phosphogypsum was greater than that of the phosphogypsum. This indicates that the permeability of the subsurface material was less than that of the phosphogypsum. Thus, if trace elements were leached from the phosphogypsum, their concentrations should be increased in the subsurface material.

Minor Components

Table 5 gives the concentrations of minor components in the phosphogypsum and in the subsurface samples. Only potassium and chromium had greater concentrations in the subsurface material than in the phosphogypsum, possibly indicating that they were leached from the phosphogypsum.

Analyses of the subsurface material, prior to the phosphogypsum being accumulated, were not available. However, the subsurface material below the phosphogypsum consists of sand, clays, and phosphate rock. The concentrations of trace elements in the clays and phosphate rock, shown in table 6, may be used to estimate the concentration of trace elements present in the soil before the phosphogypsum was placed on top of it. For example, from table 4, it can be seen that phosphate rock comprises 20 pct of the subsurface material. The concentration of a trace element previously present in the soil, as a result of the presence of phosphate rock, can be estimated as 20 pct of the value of the trace element shown in table 6 (column 3).

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[4] Gypsum = pct $SO_3/0.465$; the factor 0.465 = fraction of SO_3 in gypsum. Sand and clay = pct SiO_2 + acid insoluble. Phosphate rock = pct $P_2O_5/0.33$; the factor 0.33 is the fraction of P_2O_5 in typical central Florida phosphate rock. Percentages were converted to the dry basis for these calculations.

TABLE 3. - Analyses of samples as received, major components

Samples	A1-2	B1-2	F1-2	F2-2	H2-2	Avg
PHOSPHOGYPSUM						
Sample depth ft..	86-88	136-138	20-21	20-22	67-72	NAp
Analyses, pct:						
Moisture[1]	2.9	3.0	5.5	12.8	17.8	8.4
Combined water	18.8	14.4	17.9	15.1	15.3	16.3
Silicon dioxide and acid insoluble	3.2	17.7	4.5	4.5	6.2	7.2
Calcium oxide	31.1	26.9	29.4	28.0	25.1	28.1
Sulfur trioxide	42.0	31.9	40.2	38.3	34.4	37.4
Phosphorus pentoxide	0.8	3.7	0.6	0.5	0.5	1.2
Aluminum	0.3	0.1	0.1	0.1	0.1	0.1
Chlorine	0.0	0.0	0.0	0.0	0.0	0.0
Fluorine	0.2	0.8	0.6	0.5	0.5	0.5
Iron	0.0	0.1	0.1	0.0	0.1	0.1
Magnesium	0.0	0.0	0.0	0.0	0.0	0.0
pH	4.5	4.5	4.5	5.3	4.6	4.7
Ratio, moles calcium oxide/moles sulfur trioxide	1.1	1.2	1.0	1.1	1.0	1.1
MATERIAL UNDER PHOSPHOGYPSUM						
Sample depth ft..	105-113	150-151	40-42	[2]50-52	82-87	NAp
Analyses, pct:						
Moisture[1]	17.9	14.9	18.9	28.9	23.2	20.8
Silicon dioxide and acid insoluble	67.9	80.1	69.7	17.6	46.0	56.3
Calcium oxide	6.5	3.3	3.0	21.8	13.7	9.7
Sulfur trioxide	1.6	0.6	0.0	2.1	0.6	1.0
Phosphorus pentoxide	3.2	0.3	2.0	10.4	8.5	4.9
Aluminum	1.2	0.1	0.9	0.5	0.8	0.7
Chlorine	0.1	0.0	0.0	0.0	0.0	[3]0.0
Fluorine	0.5	0.1	0.0	1.1	1.0	0.5
Iron	0.3	0.3	0.2	0.7	1.1	0.5
Magnesium	0.0	0.1	0.1	1.7	0.4	0.5
pH	4.0	5.0	5.6	6.8	5.4	5.4
Ratio, moles calcium oxide/moles sulfur trioxide	5.9	7.6	[4]430	14.6	31.5	98

NAp Not applicable.

[1] This is referred to as "free water" in phosphogypsum or gypsum.

[2] This sample also contained 7.9 wt-pct CO_2.

[3] Without rounding off, this value is 0.02 pct.

[4] Based on 2.98 pct CaO and 0.01 pct SO_3.

TABLE 4. - Approximate mineral compositions of samples, dry basis, weight-percent

	A1-2	B1-2	F1-2	F2-2[1]	H2-2	Avg
PHOSPHOGYPSUM SAMPLES						
Gypsum[2]	93	71	91	94	90	88
Sand and clay[3]	3	18	5	5	8	8
Phosphate rock[4]	3	11	2	1	2	4
SUBSURFACE SAMPLES						
Gypsum[2]	4	2	0	6	2	3
Sand and clay[3]	83	94	86	25	60	70
Phosphate rock[4]	12	1	7	44	34	20

[1] The subsurface sample also contained 7.9 pct CO_2, equivalent to 25 pct limestone ($CaCO_3$).

[2] Gypsum = pct $SO_3/0.465$.

[3] Sand and clay = pct SiO_2 and acid insoluble.

[4] Phosphate rock = pct $P_2O_5/0.33$.

TABLE 5. - Analyses of samples as received, minor components

Samples	A1-2	B1-2	F1-2	F2-2	H2-2	Avg
PHOSPHOGYPSUM						
Sample depth...ft..	86-88	136-138	20-21	20-22	67-72	NAp
Analyses, μg/g:						
Arsenic	3	2	3	2	8	4
Barium	<10	<10	<10	<10	<10	<10
Cadmium	3	3	4	4	3	3
Chromium	15	20	19	21	30	21
Copper	7	11	11	7	5	8
Lead	12	13	9	7	2	9
Mercury	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Nickel	17	13	12	10	12	13
Potassium	86	42	24	20	63	47
Selenium	1	<0.5	2	<0.5	1	<1
Silver	<3	<3	<3	<3	<3	<3
Sodium	4,500	1,300	180	150	490	1,300
MATERIAL UNDER PHOSPHOGYPSUM						
Sample depth...ft..	105-113	150-151	40-42	50-52	82-87	NAp
Analyses, μg/g:						
Arsenic	3	2	2	3	5	3
Barium	<10	<10	<10	<10	<10	<10
Cadmium	3	2	2	4	3	3
Chromium	410	150	160	89	140	190
Copper	2	1	1	5	5	3
Lead	13	5	13	9	2	8
Mercury	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Nickel	8	9	2	19	14	10
Potassium	490	510	180	430	460	410
Selenium	<0.5	<0.5	<0.5	1	1	<1
Silver	<3	<3	<3	<3	<3	<3
Sodium	400	130	410	1,800	1,900	930

NAp Not applicable.

TABLE 6. - Trace element concentrations in subsurface samples, phosphate rock, and clay

Trace element	In subsurface samples,[1] μg/g	In phosphate rock[2]		In clay[2]	
		Conc., μg/g	Reference	Conc., μg/g	Reference
Arsenic	3	20	8, p. 55	13	8, p. 55
Barium	<10	70	8, p. 55	580	8, p. 55
Cadmium	3	30	8, p. 71	.3	8, p. 55
Chromium	190	100	8, p. 55	750	9, p. 226
Copper	3	10	8, p. 55	45	8, p. 55
Lead	8	50	8, p. 71	20	8, p. 55
Mercury	<.5	7	8, p. 55	.3	9, p. 226
Nickel	10	15	8, p. 55	68	8, p. 55
Potassium	410	2,000	8, p. 71	30,000	9, p. 226
Selenium	<1	7	8, p. 71	.6	8, p. 55
Silver	<3	5	8, p. 55	.1	8, p. 55
Sodium	930	5,900	8, p. 71	10,700	9, p. 226

[1] Averages, table 5.

[2] Maximum values in references cited.

The values in table 6 are the maximum values reported in the references cited. The results show that the actual concentrations of As, Ba, Cd, Pb, Hg, K, Se, Ag, and Na in the subsurface samples are lower than the concentrations of these metals estimated to be present with phosphate rock. Since these metals also are present in the clay, their estimated total concentration in the subsurface soil would be even greater. Therefore, these elements have not been leached from the phosphogypsum stacks. Copper also shows no significantly increased concentration, but nickel and chromium do. The nickel concentration is increased from 3 to 10 µg/g and the chromium from 20 to 190 µg/g in subsurface samples compared to the background estimates for phosphate rock. Therefore, the chromium and nickel content of the clay also must be accounted for.

The same type of comparative projections can be made for the trace elements contained in the clay fraction. The amount of clay present is not as easily or as accurately determined as the phosphate rock. It can be estimated from the Fe, Mg, K, Si, and Na present, remembering that much of the Si exists as sand (SiO_2) and must be excluded from the estimate. The clay fraction was estimated by dividing the concentrations (on a dry basis) of Al, Fe, Mg, K, and Na (tables 3 and 5) by the concentrations of each of these elements in normally occurring clay (table 6). This produced an average value of 16 pct clay in the subsurface samples.

Taking 16 pct of the background concentrations (table 6, column 4) gives 7 µg/g Cu and 11 µg/g Ni. This exceeds the actual level found in the subsurface samples. Therefore, Cu and Ni have not been leached from the phosphogypsum. The total chromium background (using columns 3 and 4 in table 6) was estimated to be 140 µg/g. Actually, 190 µg/g was found in the subsurface sample, but the difference, 50 µg/g, was not considered significant because it was less than one standard deviation of the average of the subsurface chromium analyses.

It was concluded that none of the metallic elements would be leached from the phosphogypsum.

Radium Analyses

Results of the radium analyses are shown in table 7. The samples tested by the two different laboratories were identical. EPA analyzed its samples by the emanation method, while the Oak Ridge National Laboratory used the germanium-lithium counting technique. The radium concentration in the phosphogypsum averaged 22.1 pCi/g, and the radium concentration in the subsurface material averaged 8.6 pCi/g.

Statistical analysis of the radium data is shown in the analysis of variance (ANOVA), table 8. At the 99-pct confidence level, these results show a significant difference between the radium concentrations in phosphogypsum and in the subsurface material. They show no significant differences among the cores or between the Oak Ridge and EPA results. The standard error of measurement was 4.68 pCi/g for 20 analyses. This is near the standard error of 4.52 pCi/g for 89 radium analyses previously reported (7). These standard errors are both very near the 5 pCi/g proposed by the EPA as a maximum for radium in hazardous wastes and would be difficult to accurately assess in practice.

The background concentrations of radium in the subsurface material, prior to the creation of the phosphogypsum piles, can be accurately estimated since long-term data are available (8, 12). Interest in radioactivity in Florida dates back to 1942-48, when there was an urgent need to find domestic sources of uranium. In addition, there has been environmental concern about radium in Florida for the last 20 yr, and considerable data have been published, some of which are shown in table 9.

TABLE 7. - Radium analyses, dry basis

Samples	A1-2	B1-2	F1-2	F2-2	H2-2	Avg
PHOSPHOGYPSUM						
Sample depth...ft..	86-88	136-138	20-21	20-22	67-72	NAp
Radium, pCi/g:						
ORNL[1]	18.2	9.2	41.3	19.8	24.6	22.6
EPA[2]	15.7	10.4	54.1	16.6	11.3	21.6
Avg	17.0	9.8	47.7	18.2	18.0	22.1
MATERIAL UNDER PHOSPHOGYPSUM						
Sample depth...ft..	105-113	150-151	40-42	50-52	82-87	NAp
Radium, pCi/g:						
ORNL[1]	11.2	1.5	2.1	20.6	11.0	9.3
EPA[2]	9.9	1.7	2.7	13.9	11.4	7.9
Avg	10.6	1.6	2.4	17.3	11.2	8.6

NAp Not applicable.

[1] Analyzed by the Oak Ridge National Laboratory, Oak Ridge, TN.

[2] Analyzed by EPA Radiation Facility, Montgomery, AL.

TABLE 8. - Analyses of variance of radium data

(Standard error = 4.68 pCi/g)

Source of variation[1]	Degrees of freedom	Sum of squares	Mean squares	F ratio
G/S	1	913.952	913.952	41.71
CORE	4	784.053	196.013	8.95
LAB	1	6.962	6.962	.32
G/S:CORE[2]	4	1,292.803	323.200	14.75
G/S:LAB[2]	1	.162	.162	.01
CORE:LAB[2]	4	108.133	27.033	1.23
Error	4	87.643	21.910	NAp
Total	19	3,193.708	NAp	NAp

G/S In phosphogypsum versus material under phosphogypsum.

CORE Among cores A1-2 through H2-2.

LAB Oak Ridge analyses versus EPA analyses.

NAp Not applicable.

[1] Comparisons of radium concentrations.

[2] Interactions among main factors.

TABLE 9. - Representative radium concentrations in Florida phosphate materials

Material	Radium, pCi/g
Background soil	1.5
Silt	1.1
Beach sand	.9
Reclaimed soil	10 -30
Overburden (excluding leach zone)	10
Leach zone material	40
Matrix	40 -60
Wet phosphate rock	29 -42
Dry phosphate rock[1]	38 -48
Sand tailings	6.2- 8.8
Gypsum	21 -33

[1] Source: National Academy of Sciences (8, p. 71); all others from EPA (12, p. 1.53).

The material under the phosphogypsum piles consists of sand, clay, and phosphate rock. From the percentages of each of these materials (table 4) and concentrations of radium in each material, the concentrations of radium in the subsurface material may be calculated. This is shown in table 10. This method is analogous to the one used above to determine the background concentration of trace elements. These data were statistically analyzed (ANOVA and F-tests) for the background versus the measured radium concentrations under the phosphogypsum piles. No significant differences were found, and it was concluded that radium was not leached from the phosphogypsum.

TABLE 10. - Radium concentration in material under phosphogypsum piles, dry basis, pCi/g

Source of radium	Samples					Avg
	A1-2	B1-2	F1-2	F2-2	H2-2	
From gypsum[1]	0.7	0.2	0.0	1.0	0.3	0.4
From sand[2]	.7	.8	.8	.2	.5	.6
From phosphate rock[3]	4.6	.4	2.7	16.7	12.9	7.5
In material under phosphogypsum piles:						
Background[4]	6.0	1.4	3.5	17.9	13.7	8.5
Observed[5]	10.6	1.6	2.4	17.3	11.2	8.6

[1] Percent gypsum (table 4) ÷ 100 × (pCi/g Ra in gypsum, table 7).

[2] Percent sand and clay (table 4) ÷ 100 × (pCi/g Ra in sand = 0.9).

[3] Percent phosphate rock (table 4) ÷ 100 × (pCi/g Ra in dry phosphate rock = 38).

[4] Sum of radium from gypsum, sand, and phosphate rock.

[5] From table 7.

PERMEABILITY

Table 11 gives the permeability data for seepage of water through phosphogypsum. The data were fitted by least squares linear regression to equation 1:

$$\ln h = a + b\,t, \qquad (1)$$

in which h is the water height in inches at time, t, in hours, and a and b are coefficients determined by the linear regression. The results gave

$a = 3.098$ in ln (inches)

$b = -1.120 \times 10^{-2}$ in hours^{-1}.

The correlation coefficient of the linear regression was 0.9999. The permeability, P, of the phosphogypsum, derived from equation 1 and Darcy's law (14), is given in equation 2:

$$P = -bL, \qquad (2)$$

in which b is the coefficient in equation 1 and L is the length, 8.37 in, of the phosphogypsum column. The permeability was 0.094 in/hr of seepage.

X-RAY DIFFRACTION

The X-ray diffraction analyses of water-soluble material from phosphogypsum showed only the presence of gypsum and a trace of hemihydrate. The sensitivity of this analysis was not sufficient to identify compounds of the trace elements.

TABLE 11. - Permeability data for water seepage through phosphogypsum

Time (t), hr	Water height (h),[1] in
0	22.05
18.53	18.07
42.67	13.82
63.44	10.91
71.25	9.92

[1] Height of water from bottom of phosphogypsum column.

NOTE.--Length (L) of phosphogypsum column = 8.37 in.

NEUTRON ACTIVATION ANALYSES

Five phosphogypsum samples were analyzed by neutron activation analysis. This yielded quantitative results and the standard deviations for the concentrations of 44 elements. These analyses are presented in table 12.

TABLE 12. - Neutron activation analyses of phosphogypsum[1] from Florida, μg/g

Element	Average	Std. dev. of avg
Aluminum	2,000	540
Antimony	.20	.03
Arsenic	0.76 - .94	0.26 - .32
Barium	<210	<24
Bromine	<.92	<.12
Calcium	21,000	5,700
Cerium	49	5.4
Cesium	.03 - .07	.01 - .02
Chlorine	<150	<4.7
Chromium	6.0	1.4
Cobalt	.58	.15
Copper	<82	<9.6
Dysprosium	<3.5	<.20
Erbium	<330	<9.7
Europium	1.5	.17
Gadolinium	130 - 170	51 - 59
Gallium	<3.0	<.26
Gold	.002- .013	.001- .002
Hafnium	1.9	1.0
Indium	<.14	<.005
Iodine	.90 - 3.8	.20 - .90
Iron	860 - 1,000	300 - 600
Lanthanum	39	4.6
Magnesium	<940	<27
Manganese	25	14
Mercury	.28 - .40	.25 - .28
Molybdenum	2.2 - 11	1.4 - 2.2
Neodymium	33	4.1
Potassium	200 - 230	83 - 94
Rubidium	.72 - 3.2	.45 - .96
Scandium	<.40	.16
Selenium	.72 - 2.1	.44 - .72
Silver	<1.3	<.64
Sodium	520	79
Strontium	600	67
Tantalum	.12	.042
Terbium	1.0	.14
Thorium	1.9	.65
Titanium	440	140
Tungsten	<.91	<.060
Uranium	9.6	2.9
Vanadium	1.8 - 4.0	.50 - 1.8
Ytterbium	2.6	.45
Zinc	<340	<21

[1] 5 samples, each a composite of cores of the depths shown: A1, 0-70 ft; B1, 0-100 ft; E, 0-90 ft; F, 0-30 ft; and H, 0-80 ft.

FACTORS INVOLVED IN LEACHING

To help explain the results of this study and to aid in predicting the future stability of phosphogypsum stockpiles, the hydrology associated with the piles and the solubility and absorption of trace elements and radium were considered. How well the objectives of this investigation were met is also briefly considered.

HYDROLOGY ASSOCIATED WITH PHOSPHOGYPSUM PILES

Phosphogypsum stockpiles in Florida are 50 to 528 acres in area, averaging 227 acres (7). The piles are formed by pumping phosphogypsum slurries from phosphoric acid plants to a system of ditches which direct the slurry within the piles. The slurries are directed to subdivided, diked areas where the phosphogypsum rapidly settles. When the phosphogypsum builds up in an area, the dikes are adjusted to redirect the slurry to another area. In this manner terraces of phosphogypsum are formed. Figure 2 shows an interior-diked phosphogypsum pile. The clear supernatant water from the slurries of the phosphogypsum flows by gravity to holding ponds and is then reused.

These slurry areas make up only a small part of the phosphogypsum stockpile areas, and most of the remaining pile areas are fairly dry. Leaching in the settled portion of the pile would be due to rainwater passing downward through the pile.

Rainfall at Lakeland, FL, for 1974 was 44 in. Of this amount, 26 in fell during a 72-hr period. There were 24 periods of

FIGURE 2. - Interior-diked phosphogypsum pile.

rain of 3-hr duration each, averaging 1.07 in of rain (15). The Soil Conservation Service (SCS) method (3) of estimating the quantity of runoff water was applied, resulting in 7 in/yr of runoff. Thus, the net amount of rainwater available to infiltrate the phosphogypsum was 37 in. in 1974. However, 1974 was an unusually dry year. Normal annual rainfall in the phosphate region is about 55 in. Using the same runoff for a normal year results in a net available rainwater of 48 in.

Evaporation usually exceeds rainfall on an annual basis in the Florida phosphate region (15). However, the infiltration rate of water into dry soil or phosphogypsum is about 0.50 in/hr (3). This greatly exceeds the evaporation rate. Once moisture has penetrated into the piles, there is little evaporation from any appreciable depth. Taking a conservative viewpoint, evaporation was considered to be zero, so that the net water available to percolate through the phosphogypsum remains 48 in/yr for a normal year.

The sample used in the laboratory permeability test had the same characteristics as the phosphogypsum in the piles. It was formed by settling a phosphogypsum slurry, followed by compaction, which is the same way the stockpiles are created. The permeability figure that resulted from the tests was the saturated hydraulic conductivity since the sample was completely immersed in a column of water during the test. However, phosphogypsum in the piles is not saturated with water but contains an average of about 15 pct moisture. Permeability decreases drastically with decreases in moisture content because of the loss of water head. The unsaturated hydraulic conductivity would be 10 pct or less of the saturated value (13), or approximately 0.009 in/hr (6.6 ft/yr).

Seepage of water through the piles is not uniform. It is greatest during a rain but almost ceases during dry periods. This results in irregular moisture profiles in the piles, with wet and dry layers alternating within the piles. This moisture pattern has been observed previously (7).

The solubility of gypsum is 0.26 pct, and its density is 2.32 g/mL. From this, the amount of phosphogypsum dissolved by rain was calculated to be a layer only 0.054 in thick for each 48 in, or year, of rain. At this rate it would require 6,600 yr of normal rainfall to dissolve a 30-ft pile of phosphogypsum.

The normal annual amount of rainfall and the rate of seepage are sufficient to leach radium and the trace elements. However, this does not occur. The rate of movement of radium and trace elements is much less than the rate of seepage. The U.S. Nuclear Regulatory Commission reported (13) that radium moves at 1/215 times the seepage rate. This was radium from a uranium tailings pond seeping through alluvium soil. The factor of 1/215 is directly dependent on the absorption of radium by the soil. Radium sulfate has a solubility of only 2.1×10^{-6} pct, is in the same crystal system as gypsum, and would be strongly absorbed by gypsum. Its rate of movement through gypsum would be at least as slow as its rate of movement through soil, or less than 6.6/215 or 0.03 ft/yr. It would require 2,300 yr for radium to migrate through a 70-ft phosphogypsum stack, and by then the radium would have disintegrated to 37 pct of its original concentration, or 7.8 pCi/g. For comparison, EPA regulations on uranium tailings allow a maximum concentration of radium--226 of 15 pCi/g averaged over 15-cm-thick layers of soil more than 15 cm below the surface (2).

SOLUBILITY OF COMPOUNDS OF TRACE ELEMENTS

Evaporation of the leach water from 1,000 g of phosphogypsum and X-ray diffraction of the resulting crystals did not identify any compounds of trace elements. Trace elements may exist as sulfates, such as mercuric sulfate, or as calcium salts, such as calcium selenate, in equilibrium with a saturated solution of calcium and sulfate ions from gypsum. Further isolation of trace elements by extraction, precipitation, ion exchange, or other means would so alter this equilibrium that the original amounts and types of compounds present would not be determined. Literature studies of phase equilibria in saturated gypsum solutions were used to identify possible trace element compounds.

Many compounds may be present in phosphogypsum piles, such as silicates, fluorides, phosphates, or chlorides. However, sulfate and calcium compounds would predominate because of the large excess of calcium and sulfate ions from the phosphogypsum. The specific compounds considered in this report are listed, by their formulas, in table 13. These are all sulfates except the calcium compounds of arsenate, chromate, and selenate, which are the most probable compounds of these elements present. Potassium is considered as $K_2SO_4 \cdot CaSO_4 \cdot H_2O$ (syngenite), identified as the solids phase present in saturated $K_2SO_4 \cdot CaSO_4$ solutions (4). Most of the solubilities were taken from Seidell (10).

TABLE 13. - Comparison of total and leachable trace elements in phosphogypsum

Element	Average, µg/g[1] Total	Average, µg/g[1] Leached	Leached, pct of total	Absorbed, pct of total[2]
Arsenic	[3]0.85	[4]0.24	28	72
Barium	[3]105	[4]3.2	3	97
Cadmium	[5]0.59	[4]0.28	47	53
Chromium	[3]6.0	[4]0.80	13	87
Copper	[5]4.9	[5]0.25	5	95
Lead	[5]1.3	[4]0.36	28	72
Mercury	[3]0.34	[4]0.012	4	96
Nickel	[5]6.3	[5]0.97	15	85
Potassium	[5]90	[5]47	52	48
Selenium	[3]1.4	[4]0.060	4	96
Silver	[3]0.67	[4]0.96	([6])	([6])
Sodium	[5]404	[5]204	50	50

Element	Axial ratios, A/A gyp.[7]	Solubility, pct as element[8]	Compounds whose axial ratios and solubilities were considered
Arsenic	1.0	0.13	$CaHAsO_4 \cdot 2H_2O$
Barium	2.0	.00023	$BaSO_4$
Cadmium	3.0	24	$CdSO_4 \cdot 8/3H_2O$
Chromium	1.7	5.6	$CaCrO_4 \cdot 2H_2O$
Copper	1.6	7.4	$CuSO_4 \cdot 5H_2O$
Lead	2.0	.00031	$PbSO_4$
Mercury	1.8	3.40	$HgSO_4$
Nickel	2.4	11	$NiSO_4 \cdot 7H_2O$
Potassium	3.3	1.4	$K_2SO_4 \cdot CaSO_4 \cdot H_2O$
Selenium	1.0	3.0	$CaSeO_4 \cdot 2H_2O$
Silver	2.0	.56	Ag_2SO_4
Sodium	3.0	7.1	$Na_2SO_4 \cdot 10H_2O$

[1] Averages from samples D and F for Na, K, Cu, and Ni. Averages from samples A1, B1, E, F, and H for all other elements.

[2] 100 minus percent leached.

[3] Analysis by neutron activation.

[4] EPA extraction procedure.

[5] Analysis by atomic absorption.

[6] Indeterminate.

[7] Crystallographic ratios A-axial ratio/A-axial ratio of gypsum. A gyp. = 0.413.

[8] Solubilities of compounds in the last column times fractions of elements (in the first column) in the compounds.

The percent leached is determined by taking the quantities of each trace element leached, times 100, divided by the total quantities present. These quantities are also presented in table 13. There is excellent linear correlation between the solubilities of copper, nickel, and cadmium sulfates and their respective percentages leached. The correlation coefficient was 0.9998. Increasing solubility correlated highly with a greater percentage leached. The anions arsenate, chromate, and selenate yielded a linear correlation coefficient of -0.64, and Ba, Cd, Cr, Cu, Hg, Ni, and Se gave a coefficient of 0.89. Except for barium and lead, whose sulfates are very insoluble, the moisture content of phosphogypsum would supply sufficient water to dissolve all of the trace elements listed in table 13. Solubility would not be a limiting factor in leaching trace elements, although barium and lead would require water seeping through the phosphogypsum stockpiles to supply sufficient water to dissolve their sulfates.

ABSORPTION OF TRACE ELEMENTS ON PHOSPHOGYPSUM

Absorption of ions from a solution, by a solid in contact with the solution, is enhanced if both the solid and liquid phases contain the same ions. Molecular absorption may occur if the molecules in solution will fit into the crystal lattice of the solid.

All of the compounds in table 13 contain either calcium or sulfate ions, in common with gypsum. The crystallographic lattice dimensions and axial ratios of each of these compounds were compared to those of gypsum. Data were obtained from the Powder Diffraction Standards Data File (6). The conventions stated by Dana (5) were used in selection of axial lengths corresponding to the a, b, and c axes. For orthorhombic and triclinic systems, the c axis is shorter than the a axis, and the a axis is shorter than the b axis, or $c < a < b$. For monoclinic systems, the c axis is shorter than the a axis dimension, or $c < a$. The A axial ratio is the quotient of the a axis dimension divided by the b axis dimension. In this report the A axial ratios of the compounds of the trace elements were divided by the A axial ratio of gypsum to give a number for each compound, indicative of the extent to which the crystal lattice of the compound matched that of gypsum. These numbers are listed in table 13 under the column "Axial ratios, A/A gyp." The percent absorbed is defined as 100 minus the percent leached and is also given in table 13. These data were fitted to equation 3

$$S = 48.7 + 53.3 R - 16.7 R^2, \qquad (3)$$

in which S equals percent absorbed and R equals the axial ratio relative to gypsum as defined. The correlation coefficient was 0.88, and the standard error of estimate was 10-pct absorption. This data indicate that absorption is a major factor.

Radium sulfate has an axial ratio relative to gypsum of 1.93. From equation 3, the absorption of radium by phosphogypsum would be 89 pct of the amount of radium originally present. This indicates that very little radium would be leached.

DISCUSSION

The three objectives of this investigation were to determine (1) if the phosphogypsum piles were hazardous toxic wastes, (2) if toxic elements were leached from phosphogypsum, and (3) if radium was leached.

The first objective involved performing the standard EPA extraction procedure and comparing the results with the EPA allowable concentrations. The findings showed that the phosphogypsum was not toxic.

The second objective involved comparing the estimated background concentrations of trace elements with the concentrations found in the subsurface samples. A difficulty encountered was in establishing the background concentrations. A firm estimate of these background concentrations was afforded through P_2O_5 analyses of the samples. This established the amounts of phosphate rock in the samples. Since concentrations of trace elements in phosphate rock and the amounts of phosphate rock in the subsurface samples were available, the trace element concentrations in the background could be estimated. On this basis alone, only nickel and chromium may be leached. The same method of estimating background concentrations was applied using clay. It showed that nickel and chromium were not leached. It was concluded that toxic element concentrations were below EPA standards and were not being leached from phosphogypsum stockpiles.

The third objective was to determine if radium was being leached. Background concentrations of radium in many materials present in the phosphate mining area have been previously determined. Using these data, it was found that radium concentrations in phosphogypsum significantly exceeded those in the subsurface samples. Also the radium concentrations in the subsurface samples were only equal to background. This indicated that radium was not leached.

CONCLUSIONS

1. Phosphogypsum stockpiles in Florida are not hazardous toxic wastes.

2. Trace elements are not leached from phosphogypsum stockpiles.

3. Radium is not leached from phosphogypsum stockpiles.

4. The standard error of measurement of radium concentration was 4.7pCi/g.

5. Absorption of trace elements and radium by phosphogypsum is the major reason for their not being leached.

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☆U.S. GOVERNMENT PRINTING OFFICE: 1983-605-015/34