

Review article

Environmental impacts of phosphogypsum**P.M. Rutherford, M.J. Dudas*, R.A. Samek***Department of Soil Science, University of Alberta, Edmonton, Alberta T6G 2E3, Canada*

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Abstract

Phosphogypsum is an acidic by-product from the phosphate fertilizer industry. Large quantities are produced world-wide and it is estimated that by the year 2000 up to 280 million tonnes will be produced annually. Although phosphogypsum is mainly calcium sulfate dihydrate, it contains elevated levels of impurities which originate primarily from the source phosphate rock used in P fertilizer production. The main environmental concerns associated with phosphogypsum are: (i) movement of fluoride, sulfate, total dissolved solids, certain trace elements, and radionuclides from the U-238 decay series below phosphogypsum stacks into groundwater supplies; (ii) radon-222 exhalation which may pose a health risk to workers on the site or people living close to stacks; (iii) acidity; and (iv) radon-222 exhalation from soil into residential homes when agricultural land previously treated with phosphogypsum is converted to residential usage. In order to fully understand the environmental impact of phosphogypsum, it is necessary to understand the geochemical and hydrological processes that control the composition of phosphogypsum leachates and the attenuation of environmentally sensitive chemical species when these leachates enter soil environments. This article will review the chemistry of phosphogypsum and the environmental concerns associated with phosphogypsum that is stockpiled in waste repositories or is used as an agricultural soil amendment.

Key words: By-product gypsum; Radon; Natural-occurring radioactivity; Heavy metals; Fluoride; Waste management

1. Introduction

Phosphogypsum is an acidic by-product produced by the phosphate fertilizer industry during the production of phosphoric acid from phosphate rock. The by-product is composed mainly of gypsum and the phosphorus content is usually below 1%. Levels of fluoride, certain natural-occurring radionuclides and trace elements are relatively high and there is concern that the material may

pose a negative impact on the environment. World-wide production of phosphogypsum was 120–150 million metric tonnes in 1980 (Carmichael, 1988) and it is estimated that if historic trends continue, production will increase to 220–280 mmt by the year 2000 (Ferguson, 1988). A study in 1981 showed that of the phosphogypsum produced, 14% is reprocessed, 58% is stored and 28% is dumped into water bodies (Carmichael, 1988). The objective of this review is to summarize the literature dealing with phosphogypsum, with emphasis on the chemistry of phosphogypsum and

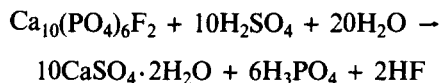
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the concerns which may arise when phosphogypsum leachates come in contact with the terrestrial environment.

Large amounts of phosphogypsum are dumped, often into water supplies throughout the world. The Djorf Lasfar plant in Morocco pumps 25 000 tons/day of phosphogypsum into the Atlantic Ocean when operating at nominal capacity (Becker, 1989). Readers interested in the environmental consequences of dumping into water should consult articles by Becker (1989) and van der Heijde et al. (1988, 1990). Readers should refer to other reviews (Arman and Seals, 1990; Novikov, 1990) for more information on the possible utilization of phosphogypsum in engineering and chemical industries.

2. Phosphoric acid production

Phosphoric acid, which is used in phosphate fertilizer production, can be produced either by: (i) the electric furnace process, which uses electrical energy to produce elemental P as a first stage; or (ii) the wet process using sulfuric acid attack. Currently, the wet process accounts for over 90% of phosphoric acid production (Becker, 1989). Phosphate rock, which is composed mainly of apatite, is treated with concentrated sulfuric acid and water to produce gypsum, phosphoric acid and hydrogen fluoride. The most common process results in the production of calcium sulfate dihydrate:



Once crystallized, the gypsum is separated from the liquid phase by filtration, mixed with water and sluiced to a disposal area or a holding area. The acidic process water is recycled. Hydrofluoric acid reacts with undissolved silicate impurities in phosphate rock to produce silicon tetrafluoride (SiF_4), which hydrolyzes to form fluorosilicic acid (H_2SiF_6). High temperatures produced during processing may allow the F acids to decompose forming gaseous SiF_4 and HF. These are usually recovered as fluorosilicic acid (H_2SiF_6) by absorption in water using scrubbers.

Phosphate rock is usually treated in a physical process called beneficiation, prior to acid treatment in order to concentrate the P content of the ore (Becker, 1989). Beneficiation often involves concentration by washing, screening and flotation (Roessler, 1979a). Calcination, the crushing of rock and heating to 910°C , may be required to reduce the organic content down to approximately 1% prior to acidulation (Norris, 1969; McClellan and Gremillion, 1980).

Approximately 5 tonnes of phosphogypsum are produced per tonne of phosphoric acid (P_2O_5). The degree of calcium sulfate hydration depends on the operating acid concentration and temperature (Witkamp and van Rosmalen, 1986), and may increase during transport and storage of the phosphogypsum. The dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) phosphoric acid process, which is the most common (Yarnell, 1987), produces 28–30% acid. The hemihydrate process ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$), relatively widely used in Europe, Japan and Africa, produces a purer phosphoric acid product with higher P_2O_5 concentration (Kouloheris, 1980). Various modifications to the hemihydrate process have been adopted by companies to produce acid concentrations between 32 and 52%. Details of various wet phosphoric acid processes are summarized by Becker (1989) and Kouloheris (1980).

2.1. Chemical and mineralogical composition of phosphate rock

Phosphate ore partly determines the nature of the phosphorus fertilizer and phosphogypsum. Phosphate ores are of sedimentary, or of igneous and metamorphic origin. Sedimentary phosphates, also known as phosphorites, represent about 85% of known phosphate rock (Habashi, 1980). The most easily mined deposits are from the great sedimentary basins which formed approximately 70 million years ago and are associated with matter from living organisms (Becker, 1989). Phosphate ores are subject to wide compositional variation and differences in quality. Apatite is the principle phosphate mineral in most phosphate deposits (Lehr and McClellan, 1972). Becker (1989) presents the chemical composition of phosphate rock concentrates from a variety of sources. Major components are CaO (29–54%), P_2O_5 (24–40%),

SiO₂ (0.1–14%), F (1.3–4.1%), CO₂ (0.2–7.3%), SO₃ (0.0–3.3%), Al₂O₃ (0.2–1.8%), Fe₂O₃ (0.1–2.6%), MgO (0.0–2.2%) and Na₂O (0.2–1.5%). Phosphorites contain approximately 10% quartz, 5% muscovite-illite, 2% organic matter, 1% dolomite-calcite, 1% iron oxide, and 1% other components (Gulbrandsen, 1967). The most common Fe-Al oxides and hydroxides identified in sedimentary phosphate rock are goethite, limonite, bauxite minerals and barbosolite (McClellan and Gremillion, 1980). Minor components include fluorite, zircon, tourmaline, montmorillonite, kaolinite, sphene and pyrite (Gulbrandsen, 1967). Other accessory minerals include titanium minerals such as rutile, ilmenite, anatase and perovskite (McClellan and Gremillion, 1980).

Francolite is the amorphous form of apatite in sedimentary phosphorites. Igneous fluorapatite has the formula Ca₅(PO₄)₃F but francolite exhibits more elemental substitutions (Osmond et al., 1985; McClellan and Lehr, 1969). Apatite varies greatly in physical, chemical and crystal properties (Lehr and McClellan, 1972). The most common apatites are carbonate apatites with isomorphous substitution of carbonate and F (CO₃F groups) for phosphate and minor substitution of Ca with Na and Mg atoms (McClellan and Lehr, 1969; Lindsay et al., 1989).

The enrichment of trace elements in phosphorites is best compared relative to shale, a common marine rock and the most common surficial rock (Altschuler, 1980). Compared to shale, the trace elements enriched in the average phosphorite are Cd (60×), U (30×), Ag (30×), Y (10×), Se (8×), Yb (5×), Mo (4×), La (4×) and Sr, Pb and Zn (each 2×). The rare earth elements, except for Ce, also exhibit enrichment relative to shale (Altschuler, 1980). The elements depleted are Li (13×), Ti (7×), Hg (7×), B (6×), Ga (5×), Co (3×) and Sn and Zr (each 2×) (Altschuler, 1980). Tooms et al. (1969) compared the elemental composition of phosphates from a variety of sources and concluded that relative to average crustal abundances, As, Cr, and Sn were enriched and Ba, Cu, Mn and Ni were depleted. Gold and Th concentrations appear to be similar in phosphorites relative to shales and Bi is enriched (Altschuler, 1980). Enrichment of Bi may be due to substitution in apatite because

the ionic radius of the Bi³⁺ ion (0.093 nm) is close to Ca²⁺ (0.099 nm) (Altschuler, 1980).

Enrichments vary between phosphorite formations. For example, relative to shale the following trace elements are enriched in the Phosphoria formation: Ag (60×), Mo (50×), Se (20×), Nd (10×), Cr (10×), As (4×), Cu (2×) and V (2×). The following elements are depleted: Zr (6×), Mn (30×), Ba (6×) and Pb (2×) (Gulbrandsen, 1966).

Some of the elements enriched in phosphorites are known, or are theorized on crystallographic spacings, to substitute for Ca in apatite. These elements are Cd, U, Sr, Pb, Zn, Y and the lanthanides (Altschuler, 1980). Substitutions of Na⁺ for Ca²⁺ and SiO₄⁴⁻ for PO₄³⁻ maintain electrical neutrality. Small quantities of CO₃²⁻, VO₄³⁻, AsO₄³⁻ and SO₄²⁻ may substitute for PO₄³⁻ in the crystal structure (Sweeney and Windham, 1979). Silver, Se and Mo are often associated with organic matter and enrichment may be due to complexation or adsorption with organic materials, similar to reactions found for As, Cd, Cu, Ni, Sb, V and Zn (Krauskopf, 1955; Gulbrandsen, 1966), or as metallic sulfide precipitates formed under reduced conditions (Altschuler, 1980). The elements depleted in phosphorite usually either occur in relatively stable and insoluble minerals, or they possess cationic or anionic configurations which cannot fit into the apatite crystal structure.

2.2. Natural radioactivity in phosphate rock

Many phosphate ores are high in natural radioactivity relative to shale. The radioactivity originates mainly from the U-238 and Th-232 decay series (see Figs. 1 and 2) and varies with the type of phosphate rock. Uranium-235 is not as prevalent in nature as U-238 and consequently radiation originating from this decay series is not considered to be a concern. Sedimentary phosphates typically contain high U concentration and low Th concentration, but igneous phosphates typically contain low concentrations of U and an appreciable amount of Th and rare earth elements (Habashi, 1980). Radionuclide concentration in the beneficiated rock is typically 100–300% of the concentration of the unprocessed rock (Roessler 1979a). Metzger et al. (1980) reported that the specific activities of U and Th-230, and the con-

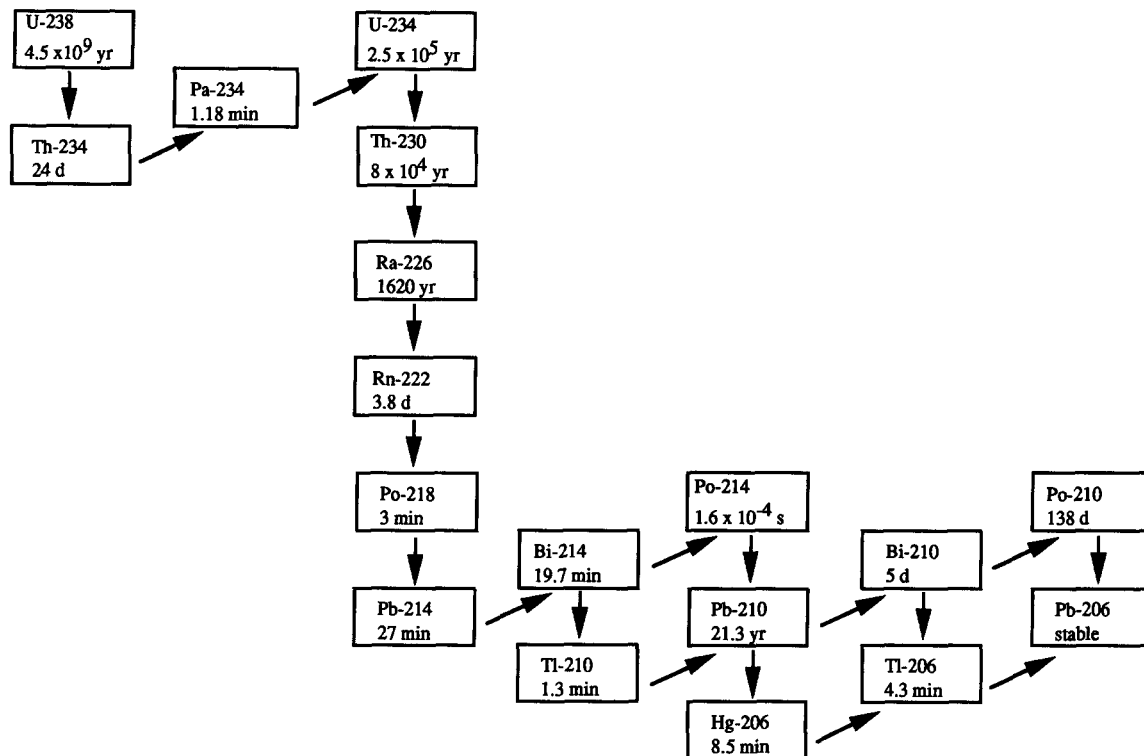


Fig. 1. Uranium-238 decay series. Diagonal arrows designate beta-decay and vertical arrows designate alpha-decay. Radionuclide half-lives are included.

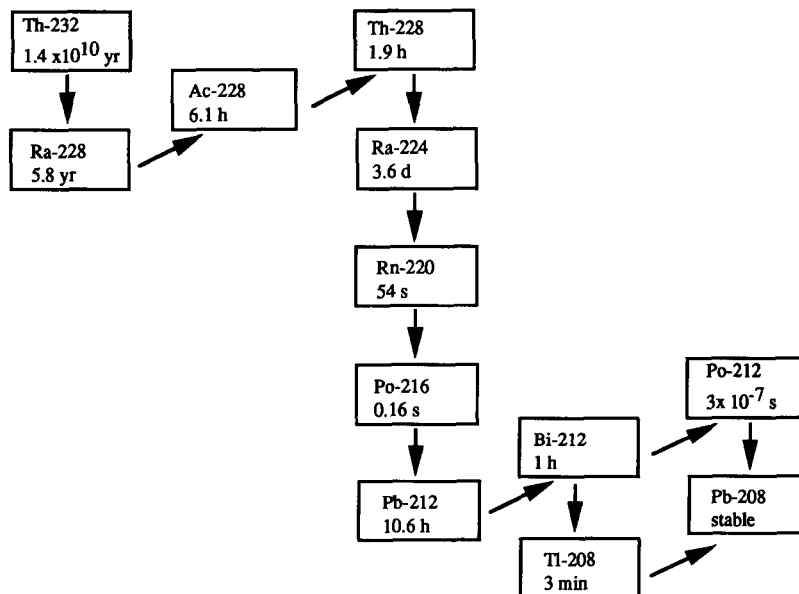


Fig. 2. Thorium-232 decay series. Diagonal arrows designate beta-decay and vertical arrows designate alpha-decay. Radionuclide half-lives are included.

centrations of Al, Cu, Mg, Na, Ti and Zn, were found to increase with decreasing particle size of beneficiated ore.

Uranium commonly exists in two oxidation states, U(IV) and U(VI). Most researchers agree that U as U(IV) replaces Ca in the apatite structure; however, some U(VI) may be adsorbed as the uranyl ion (UO_2^{2+}) onto apatite crystal surfaces (Hurst and Arnold, 1980; Burnett et al., 1988). Uranium (IV) may also be adsorbed or exist as a chemically-complexed phase on clay minerals and organics (Upchurch et al., 1991). In Florida phosphate rocks, U(IV) represents 40–90% of the 10–200 $\mu\text{g g}^{-1}$ of U (Lindeken, 1980). Menzel (1968) summarized the contents of U, Ra and Th in phosphate rocks from different sources around the world. Uranium content ranged from 3 $\mu\text{g g}^{-1}$ in ore from Chile and Ecuador islands to 399 $\mu\text{g g}^{-1}$ in ore from South Carolina. Typical soil values for U are approximately 2.7 $\mu\text{g g}^{-1}$ (Sposito, 1989).

Thorium exists in the +4 state in nature. Thorium (IV) probably substitutes for Ca in the apatite structure due to the similarity of the two ionic radii ($\text{IR} = 0.102$ vs. $\text{IR} = 0.099$ nm, respectively), although thorium may also concentrate in other compounds because it readily coprecipitates with oxidate minerals like Fe and Mn oxides. Levels of radionuclides from the Th-232 decay series are usually low in most sedimentary phosphate ores (Metzger et al., 1980).

Radium-226 is the most abundant Ra isotope in sedimentary phosphate ores. Radium-228 is present at very low concentrations because it is a product of the Th-232 decay series (Osmond et al., 1985). Menzel (1968) found Ra levels to range from undetectable in western European phosphates to $133 \times 10^{-6} \mu\text{g g}^{-1}$ ore from South Carolina. Roessler et al. (1979a) found U-238 and Ra-226 activities in Florida phosphate ore to be in approximate secular equilibrium and averaged 0.3 Bq g^{-1} in north Florida and 1.4 Bq g^{-1} in central Florida. Due to the chemical and crystallophysical properties of Ra-226 the radionuclide probably does not occupy regular lattice positions within U-bearing materials (Burnett et al., 1988). Where as U(IV) ($\text{IR} = 0.097$ nm) often substitutes for Ca ($\text{IR} = 0.099$ nm) in apatite due to the similarity of

size (Hurst and Arnold, 1980), Ra has an ionic radius of approximately 0.152 nm (Ames and Rai, 1978; Vdovenko and Dubasov, 1975), which is too large for the isomorphous replacement of Ca. Likely, Ra in phosphorite is co-precipitated with Ba and/or Sr as a sulfate compound.

A review of world-wide data on natural radioactivity in phosphate rock, products and by-products was presented in the 1977 report on the United Nations Scientific Committee of the Effects of Atomic Radiation (UNSCEAR, 1977). Guimond (1978) also reviewed the natural radioactivity associated with the phosphate industry.

3. Characteristics of phosphogypsum

3.1. Physical characteristics

Phosphogypsum has physical properties similar to natural gypsum. Particle density ranges between 2.27 and 2.40 g cm^{-3} (SENES, 1987). Bulk density within phosphogypsum stacks has been reported to range between 0.9 and 1.7 g cm^{-3} (Vick, 1977; Keren and Shainberg, 1981; May and Sweeney, 1984a). Phosphogypsum generally has a large proportion of medium to fine-grained particles. May and Sweeney (1984a) reported medium sized particles (0.250–0.045 mm diameter) to account for 36–60% of the mass of seven phosphogypsum samples. Fine particles (< 0.045 mm diameter) accounted for 2–49% of the mass. SENES (1987) reported 30% of the phosphogypsum obtained from a stack in Dunnville, Ontario to be of fine size or smaller, while 50% of the phosphogypsum was of fine size or smaller at another stack at Calgary, Alberta. The fine particle size of phosphogypsum results in a rapid dissolution rate relative to mined, natural gypsum (Keren and Shainberg, 1981). Harvie et al. (1984) estimated the solubility product for gypsum to be 2.63×10^{-5} at 25°C. Vertical hydraulic conductivity of phosphogypsum has been reported to range between 1×10^{-3} and $2 \times 10^{-5} \text{ cm s}^{-1}$ (SENES, 1987).

The free water content of phosphogypsum may vary greatly depending on how long the phosphogypsum has been allowed to drain after sluicing to the stack, and on local meteorological conditions. The free water content of phosphogypsum is often

determined by drying at 65°C for 5 h. This method may result in the loss of some water of hydration when drying occurs above 60°C. Drying at a lower temperature may be very time consuming; consequently Averitt and Gliksman (1990) recommend drying at 50°C for 5 h under vacuum.

Phosphoric acid process conditions influence the crystal morphology of phosphogypsum. It is important that the gypsum crystals produced do not have surface-to-volume ratios which are so high that they impede phosphoric acid flow during filtration (Becker, 1989). Crystal shape and size distribution determine the surface-to-volume ratio and filter cake porosity (Becker, 1989). Common gypsum shapes include needles, small thin lozenges, rhombic and X-shaped swallowtail twins, flat table-like, clusters and thick rhombic types (Becker, 1989). Ball-like clusters have the minimal surface-to-volume ratio and produce the most rapid acid flow rates. The most common shape is a table-like elongated crystal, with dimension ratios of 16:4:1 (Becker, 1989). May and Sweeney (1984a) reported that Florida phosphogypsum exhibited monoclinic crystals which were tabular and diamond-shaped. This was also found by Luther et al. 1993. Larger crystals had sides ranging between 15 and 30 μm , a thickness of 3–5 μm and a length of 20–40 μm . Solid needle shapes, hollow four-sided tubular shapes and thin flakes were also observed.

The factors which control the shape and size of the gypsum crystals formed in the reaction slurry are: (1) the type of phosphate rock; (2) phosphate rock particle size; (3) concentration of phosphoric acid; (4) solids content in the slurry; (5) excess sulfuric acid in the slurry; (6) impurities in the phosphate rock; (7) temperature; and (8) the reaction system, feed-to-volume ratios, agitation, and recirculation (Becker, 1989).

3.2. Chemical and mineralogical composition

The chemical and mineralogical characteristics of phosphogypsum depend on the nature of the phosphate ore, the type of wet process used, the efficiency of plant operation, the age of the stockpile, and any contaminants which may be introduced into the phosphogypsum at the production plant (Arman and Seals, 1990). Calcium and SO_4^{-2} dominate the composition of phosphogyp-

sum because it is approximately >90% gypsum (Berish, 1990). Phosphogypsum is acidic due to residual phosphoric acid, sulfuric acid and fluoride acids contained within the porosity. May and Sweeney (1984a) found the pH of extracts from Florida phosphogypsum to range between 2.1 and 5.5. The pH of aged and leached phosphogypsum may approach neutrality (SENES, 1987). The acidic nature of fresh phosphogypsum may keep trace elements dissolved from phosphate rock in a potentially mobile state.

Although phosphogypsum solids are mainly gypsum, many impurities are present. These include quartz, fluorides, phosphates, organic matter and minerals of Al and Fe. Using X-ray diffraction, May and Sweeney (1984a) found α -quartz to make up approximately 5% of Florida phosphogypsum. May and Sweeney (1984b) conducted X-ray analyses on the evaporites of water-soluble material from gypsum and found only gypsum and hemihydrate. The sensitivity of the analysis was not sufficient to identify trace element compounds. Luther et al. (1993) found crystalline or amorphous materials among the matrix of well-formed gypsum crystals using SEM-EDX. These minerals were dominated by Si and/or P, combined in some cases with significant amounts of Al, Na, K, Ca and/or S. The Si was attributed to α -quartz, or to feldspars in the presence of Al and Na or K. The P was attributed to residual phosphate rock. Some samples contained as much as 10% SiO_2 and 1.6% P_2O_5 . Silica is sometimes added to the liquor in phosphoric acid production to assist in the crystallization process (Beretka, 1990). Silica may also originate from sand present in process water supplies.

Major elemental composition of phosphogypsum varies according to the type of wet phosphoric acid process used (Table 1). Minor element composition may vary greatly depending on the source of the phosphate rock (Table 2). Luther et al. (1993), in part, studied the elemental composition of Alberta phosphogypsum originating from western Idaho rock and compared the results with literature values for terrestrial materials (Table 2 and 3). Relative to shale, phosphogypsum was elevated in total content of Ag, Au, Cd, Se, Sr, and some of the light rare earth elements and Y. Phospho-

Table 1

Typical major element composition (%) for phosphogypsum produced under different processes^a

Component	Dihydrate	Hemihydrate	Hemi-dihydrate
CaO	32.5	36.9	32.2
SO ₃	44.0	50.3	46.5
P ₂ O ₅	0.65	1.50	0.25
F	1.2	0.8	0.5
SiO ₂	0.5	0.7	0.4
Fe ₂ O ₃	0.1	0.1	0.05
Al ₂ O ₃	0.1	0.3	0.3
MgO	0.1	—	—
H ₂ O (Crystalline)	19.0	9.0	20.0

^aAdapted from Kouloheris, 1980.

Table 2

Content (mg kg⁻¹) of some trace elements in phosphogypsum (PG) produced from different rock phosphate sources^a; also included are literature values for terrestrial materials

Element	Florida source PG	Idaho source PG	South African source PG	Tunisian source PG	Shale ^b	Typical soil ^c
Ag	<1	1–11			0.1	0.05
As	40	<1–2			10	7.2
Au (μg kg ⁻¹)		3–15			3	
B	3	<10–30			100	33
Ba	7	20–140	140		600	580
Be	1	1–2			3	0.92
Br		1–2			5	0.85
Cd	7	9–28		40	0.3	0.35
Cl		<100–300			170	100
Co	2	<1–1		8	20	9.1
Cr		<10–70			100	54
Cu	8	10–42	103	6	50	25
Hg (μg kg ⁻¹)			<50	14000	300	90
Mn	15	<2–10			850	550
Mo	16	<1–2		5	2	0.97
Ni	2	3–15	13	15	80	19
Pb	1	3–7			20	19
Rb		<10–20			140	67
Sb	100	0.3–0.8			1.5	0.66
Se		4–67			0.6	0.39
Sr	10	610–670			400	240
Th		<1–1			12	9.4
U		6–13			3.5	2.7
V	19	10–40			130	80
Y	2	100–120	50		35	25
Zn	9	18–112	6	315	90	60
Zr	10	<10–110	185		170	230

^aFlorida source phosphogypsum from May and Sweeney (1984a); Idaho source phosphogypsum from Luther, et al. (1993); South African source phosphogypsum from Malan (1988); Tunisian source PG from Rouis and Bensalah (1990).^bFrom Krauskopf (1979).^cFrom Sposito (1989).

Table 3

Content (mg kg⁻¹) of selected rare earth elements in dihydrate phosphogypsum produced from Idaho phosphate rock^a and literature values for terrestrial materials

Element (Z) ^b	Idaho		Shale ^c	Soil ^d
	Mean	Range		
La (57)	81	69–90	40	37
Ce (58)	36	31–45	70	49
Nd (60)	36	30–46	30	46
Sm (62)	5.4	4.7–6.3	7	6.1
Eu (63)	1.2	1.1–1.4	1.4	1.9
Tb (65)	1	0.8–1.2	1	0.63
Yb (70)	2.8	2.6–3.5	3.5	2.3
Lu (71)	0.41	0.36–0.51	0.6	0.34

^aFrom Luther et al. (1993).

^bAtomic number.

^cFrom Krauskopf (1979).

^dFrom Sposito (1989).

gypsum from central Florida had greater As, Sb and Mo content than the Alberta phosphogypsum but had lower concentrations of Ag, Ba, Cd and Sr. In terms of total concentrations, May and Sweeney (1984a) said phosphogypsum could not be classified as a toxic waste because it was neither corrosive (pH was > 2 and < 12.5) and because the average total elemental concentration of elements classified as toxic by the E.P.A. (As, Ba, Cd, Cr, Pb, Hg, Se, and Ag) were less than the E.P.A. allowable toxic elemental criteria for toxic hazardous waste (Federal Register, 1980).

Levels of Y, Zr, Cu, Ba, and Ni in South African phosphogypsum were much greater than central Florida levels (Table 2). Tunisian phosphogypsum was reported to contain very high levels of Cd, Hg and Zn. Compared to Quebec standards for the

classification of contaminated soil, the phosphogypsum was slightly contaminated with Zn and Mo, but highly contaminated with Cd and Hg (Rouis and Bensalah, 1990).

Berish (1990) identified acidic process water, fluoride, radionuclides and heavy metals as possible contaminants of concern in phosphogypsum. Table 4 shows the percent transfer of trace elements from phosphate rock to phosphogypsum during the wet phosphoric acid process. Although the dihydrate process has the advantages of lower capital outlay, lower production costs, the ability of processing varying grades of phosphate rock and the capability of producing an acid from which U can be extracted (Kouloheris, 1980), the process has the major disadvantage of producing a gypsum with the most impurities. The impurities are mainly fluorine compounds (1.5–2.5%) and phosphate compounds (0.82% by wt.) (Schroeder and Gorecki, 1980). Filter cakes from the dihydrate process may contain as much as 0.5–1.0% P₂O₅. Impurities in typical hemihydrate are still relatively high and there is no method to extract U from the acid of this process (Kouloheris, 1980). The hemi-dihydrate process produces a relatively clean phosphogypsum filter cake (Table 1).

The form of major and trace elements in a solid can be attributed to a number of processes including precipitation in an essentially pure mineral

Table 4

Trace element transfer (%) from U.S. phosphate rock into phosphogypsum^a

Element	Percent transfer
Cd	30–54
Cu	64–100
Zn	20–49
Cr	3–26
V	1–100

^aAdapted from Becker (1989).

phase, fluid inclusions, co-precipitation, solid solution formation and adsorption on the surface of organic or mineral components (Luther and Dudas, 1993). Free phosphoric acid, unreacted phosphates, sodium hexafluorosilicate, sodium sulfate, fluorosilicic acid and organic compounds may adhere to the surface of gypsum crystals. Elements which substitute into the gypsum structure include Cd (van der Sluis et al., 1986; Witkamp and van Rosmalen, 1988), Sr, Mg, Na, K and Cl (Kushnir, 1980) and Se (Neal, 1990). Dicalcium phosphate, monosodium sulfate and fluorophosphates may also substitute into the crystal structure of gypsum crystals. Fluorite and fluorapatite may be the potential solubility controlling solids for F in phosphogypsum (Murray and Lewis, 1985; Jenne et al., 1980). A solid solution exists between gypsum and dicalcium phosphate because HPO_4^{2-} ions replace SO_4^{2-} ions in the gypsum lattice structure (Goers, 1980; Olmez and Erdem, 1989). Substitution of phosphate into the gypsum crystal during acidulation is reduced with higher SO_4^{2-} concentrations, longer phosphate attack times, higher reaction temperatures and high percent solids (Goers, 1980). Silicon probably exists as amorphous SiO_2 , quartz or in SiO_2 -containing minerals (Lindsay, 1979; Rai et al., 1987).

Fluorapatite contains up to 1% by mass of rare earth elements (REE) (Berdonosova et al., 1989). Phosphogypsum may be composed of 0.5% lanthanide oxides (Kijkowska et al., 1989). The REE are members of Group IIIA in the periodic table and are also referred to as the lanthanide series. They have similar chemical properties because all have a relatively stable +3 oxidation state. Yttrium is not a REE but it shares a similar chemistry with REE and is therefore often discussed with members of the REE (Henderson, 1984). Sixty to 80% of the REE present in phosphate rock may be partitioned into the phosphogypsum (dihydrate or hemihydrate) during the production of phosphoric acid (Andrianov et al., 1976; Berdonosova et al., 1989). However, there is evidence that heavy REE (Gd to Lu) may be preferentially partitioned into phosphoric acid compared to the light REE (La to Sm) during the wet phosphoric acid process (May and Sweeney, 1984b). Elements such as Ce^{3+} in the presence of Na^+ form a solid solution with

hemihydrate during crystallization [$\text{NaCe}(\text{SO}_4)_2 \cdot \text{H}_2\text{O} + \text{CePO}_4 \cdot 0.5\text{H}_2\text{O}$] – $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ (Bushuev et al., 1988). This stabilizes the hemihydrate sulfate structure and slows down the recrystallization of dihydrate sulfate during the hemi-dihydrate process (Bushuev et al., 1988).

It is not known what chemical forms many of the trace elements take in phosphogypsum, although sulfate and phosphate minerals are likely under aerobic, acidic conditions (Luther and Dudas, 1993). Possible solubility controlling solids for trace elements in phosphogypsum will be discussed in a later section.

3.3. Radionuclides and their geochemistry

Phosphogypsum is enriched in radioactivity relative to most geological and soil materials because it is derived from phosphate rock, which contains relatively high levels of naturally-occurring radionuclides. The source of radioactivity comes from two decay series originating from the two parent radionuclides, U-238 and Th-232 (Figs. 1 and 2). The U-235 or Actinium decay series also exists in nature but the shorter half-life of U-235 (7.13×10^8 years), compared to U-238 (4.51×10^9 years) and Th-232 (1.39×10^{10} years), has reduced the abundance of this U isotope over the millennia to 0.72% of total U. Thorium content in sedimentary phosphate ores is usually low (Menzel, 1968; Metzger et al., 1980) and is not considered an environmental concern except in igneous phosphate rock deposits.

In undisturbed natural deposits, the members of the U-238 decay series are in approximate radioactive equilibrium; however, some Rn-222 gas may diffuse out of the material, thereby reducing the activity of radionuclides which follow Rn-222 in the decay series. Beneficiation is a physical process which does not appreciably disrupt radioactive equilibrium but increases the radioactivity of the concentrated rock by up to 400% over the non-processed matrix (Roessler et al. 1979a; Lisachenko et al., 1987). During the wet phosphoric acid process, the radioactive equilibrium within the phosphate rock is disrupted and the radionuclides are partitioned into various phases according to their solubility (Roessler et al., 1979a; Lardinoye

et al., 1982). Uranium, Th and Pb-210 distribute primarily into the phosphoric acid while most of the Ra-226 and Po-210 partition into the phosphogypsum. Hurst and Arnold (1982) reported that 60% of the Ra-226 and 99% of the Po-210 appear in the gypsum.

Reported radionuclide activities in phosphogypsum are presented in Table 5. Radium-226 activity is usually the largest source of radioactivity in phosphogypsum although some authors have also reported high activities of U-234, U-238 and Po-210. The highest Ra-226 activities have been

Table 5
Summary of reported radionuclide activities in phosphogypsum

Location of phosphogypsum	Phosphate rock origin	Radionuclide	Mean activity (Bq kg ⁻¹)	Reference
Alberta	Idaho	Ra-226	890	Luther et al., 1993
		Th-228	5.8	Luther et al., 1993
Australia	numerous	Ra-226	500	Beretka, 1990
			451	Beretka and Mathew, 1985
		U-238	510	Beretka, 1990
		Th-232	10	
			10	Beretka et al., 1985
		K-40	20	Beretka, 1990
Florida	central Florida	Ra-226	1140 (844–1670) ^a	Guidry, 1990
			1100 (836–1230)	Horton et al., 1988 ^b
			820 (340–2000)	May and Sweeney, 1984b
			958 (780–1290)	Roessler et al., 1979a
		U-234	130 (100–180)	Horton et al., 1988 ^b
			75	May and Sweeney, 1984a
		U-235	6	
		U-238	130 (93–190)	Horton et al., 1988 ^b
			76	May and Sweeney, 1984a
		Th-227	21	
		Th-228	1	
		Th-230	113	
			190 (110–250)	Horton et al., 1988 ^b
		Th-232	3.7	May and Sweeney, 1984a
		Po-210	1030 (984–1090)	Horton et al., 1988 ^b
			1480 ^c	Roessler et al., 1986
		Pb-210	1370 (1270–1430)	Horton et al., 1988 ^b
	north Florida	Ra-226	500 (477–548)	Roessler et al., 1979a
		U-238	< 20	
Hungary	Syria	Ra-226 ^d	1093	Fourati and Faludi, 1988
		Ra-228 ^d	68	
Louisiana	not given	Ra-226	1100 (700–1700)	Laiche and Scott, 1991
Mississippi	not given	Ra-226	780	Mullins and Mitchell, 1990
		Po-210	8.1	
Sweden	Kola (USSR)	Ra-226	15	NEA, 1979
		Th-232	62	
		K-40	48	
Yugoslavia	not given	Ra-226	390	Kobal et al., 1990

^aRange.

^bActive stacks only.

^cEstimated assuming Ra-226 and Po-210 in phosphate rock were in equilibrium and 99% of Po-210 was partitioned into phosphogypsum during chemical processing.

^dEstimated assuming equilibrium between Ra-226 and Bi-214, and between Ra-228 and Ac-228.

reported in phosphogypsum originating from central Florida rock, although phosphogypsum originating from Idaho or Syrian rock may be high as well. Generally, Th radionuclides have lower specific activities than Ra-226. Phosphogypsum produced from igneous rock phosphate may have Th-232 activities which exceed those of Ra-226.

Radium-226 content in phosphogypsum exceeds levels found in fly ash and soils, however, Th-228 content is generally less in phosphogypsum than fly ash or soil. Fly ash samples from coal combustion contain approximately 100 Bq kg^{-1} of Ra-226 (Coles et al., 1978; Kobal et al., 1990). Soil Ra-226 activity is typically less than 50 Bq kg^{-1} (Myrick et al., 1983; Kiss et al., 1988; Berish, 1990), although soil formed on high U containing parent materials may be more than 50-fold greater than this (Michel, 1987). Coles et al. (1978) reported Th-228 in fly ash to be $6\text{--}20 \text{ Bq kg}^{-1}$. Kiss et al. (1988) determined Th-232 and its daughter radionuclides to have an activity of 24 Bq kg^{-1} in Saskatchewan soils.

The specific activity of various radionuclides in phosphogypsum has been well reported; however, radionuclide geochemistry in phosphogypsum has not received much attention. The geochemistry of the radionuclides present in geological materials such as phosphate rock has been summarized in several publications (Ames and Rai, 1978; Osmond et al., 1985; Burnett et al., 1988; Upchurch et al., 1991).

Natural radioactive decay can affect the chemical behavior of radionuclides. For example, alpha recoil can break chemical bonds, move the recoiled atom to a different position in a solid and may damage crystal structures (Michel, 1987). This may have an effect on the activity of solids, especially ones of colloidal size, resulting in activities which exceed one (Upchurch et al., 1991). Biological processes can have an effect on radionuclide behavior. Birch and Bachofen (1990) review the effect of microbiologically derived complexing agents on radionuclide mobility. Microbially produced organic compounds have been found to increase the solubility of some radionuclides, such as U.

Uranium. The three naturally occurring isotopes U-234, U-235 and U-238 have average percent

abundances of 0.0056, 0.72 and 99.27%, respectively, in the environment (Ames and Rai, 1978). The element is polyvalent and has complex solubility relationships depending on redox potential. Common oxidation states are +3, +4, +5 and +6, although the +4 and +6 states are the most stable (Ames and Rai, 1978).

Small amounts of U are normally contained within phosphogypsum. Most U from phosphate rock is partitioned into the phosphoric acid during the acidulation process (Roessler et al., 1979a; Hurst and Arnold, 1980); however, the partitioning is affected by redox conditions and the presence of other ions. Organic compounds in the processed phosphate rock tend to increase the U content of phosphogypsum (Gorecka and Gorecki, 1984). Uranium dissolution from phosphate rock is greater when acidulation is carried out under oxidizing conditions. Losses to the gypsum filter cake occur when unreacted rock particles are coated with gypsum or when U is substituted into the crystal lattice of the gypsum (Hurst and Arnold, 1980). Excess sulfate and fluoride may enhance the partitioning of U into the gypsum crystal. The U(IV) present in the crystal lattice of the apatite, and that formed by reduction of U(VI) by Fe(II) during acidulation, is trapped within the crystal lattice of the calcium sulfate crystals as they grow (Hurst and Arnold, 1980) because U(IV) and Ca^{2+} have very similar ionic radii (0.097 and 0.099 nm, respectively) (Gorecka and Gorecki, 1984). Thus, the presence of a large amount of Fe^{2+} may result in the transfer of as much as 80% of the U from the phosphate rock into the phosphogypsum. Uranium tends to concentrate in very small phosphogypsum particles (Gorecka and Gorecki, 1984). Under reduced conditions there is a greater transfer of U to phosphogypsum during processing. In contrast, 90–95% of U remains in the liquid phase under oxidizing conditions and in the presence of HNO_3 . Small amounts of U may be present in phosphogypsum in the form of uranyl ion (UO_2^{2+}) contained within the residual phosphoric acid which remains after filtration and sluicing to the stack. Uranium (VI) may adsorb on the surface of gypsum as UO_2HPO_4 or UO_2^{2+} may substitute for two Ca^{2+} ions on the surface of the crystal lattice (Gorecka and Gorecki, 1984).

The U content of phosphogypsum also depends on the type of wet phosphoric acid process used. The dihydrate method results in a U content of 5–25 $\mu\text{g g}^{-1}$ but the hemihydrate process results in a content of 5–100 $\mu\text{g g}^{-1}$. This difference is due to several factors. The hemihydrate has a hexagonal instead of a monoclinic unit cell structure (Turk and Bounini, 1984) and forms agglomerates and clusters which more easily accommodate U into the crystal structure (Gorecka and Gorecki, 1984). Higher temperatures and higher phosphate concentration also favor coordination into the hemihydrate.

The chemical behavior of U is affected by pH and redox conditions. Under reduced conditions and pH below 3–4, the uranous (U^{4+}) ion forms complexes with fluoride. At higher pH, uranous-hydroxy complexes form. The solubility of U(IV) species are low, but U(VI) species may be quite soluble and mobile. At pH below 5 uranyl ion (UO_2^{2+}) and uranyl fluoride dominate. Between pH 4 and 7.5 $\text{UO}_2(\text{HPO}_4)_2^{2-}$ becomes prevalent. Uranyl di- and tri-carbonate species become prevalent at higher pH. Minimum solubility of uranyl minerals occurs between pH 5 and 8.5 and sorption occurs in decreasing order to organics, ferric hydroxides, Mn- and Ti-oxyhydroxides, and clays (Osmond et al., 1985; Upchurch et al., 1991).

The distribution of U radioisotopes in the environment is affected by the radioactive decay process. As U-238 forms Th-234 alpha recoil results in some of the daughter Th-234 atoms to be ejected from the mineral crystals into pore water or air. Thus this leads to a greater enrichment of U-234, the decay daughter of Th-234, in groundwater relative to U-238 (Upchurch et al., 1991).

Radium. Radium-226 is a major source of radioactivity in phosphogypsum. This radionuclide is formed by alpha decay of Th-230 within the U-238 decay series. Radium-228 is the second most abundant Ra isotope but it is quite rare in phosphogypsum because it is formed within the Th-232 decay series which is not abundant in marine sediments.

Radium belongs to the alkaline earth elements and therefore is divalent and has similar properties to Ca, Sr and Ba. Consequently, Ra-226 is an environmental concern because it follows similar

biological pathways as Ca (Roessler, 1980). Between 70 and 90% of the Ra in the body is contained within bone (UNSCEAR, 1977).

Ra-226 probably does not co-crystallize with calcium sulfate dihydrate during phosphoric acid production because: (i) radium sulfate is very insoluble compared to calcium sulfate dihydrate, therefore almost all radium sulfate will be precipitated before the gypsum begins to precipitate; (ii) the ionic radii of Ra (IR = 0.152 nm) and Ca (IR = 0.099 nm) are so different that isomorphous substitution is unlikely; and (iii) radium sulfate (along with barium sulfate) crystallize in the rhombohedral system while calcium sulfate dihydrate crystallizes in the monoclinic system. There is a greater chance of co-precipitation of Ra-226 in the calcium sulfate hemihydrate system than with the dihydrate system because the former crystallizes in a rhombohedral system (Moisset, 1980). May and Sweeney (1984a), Beretka and Mathew (1985) and Moisset (1990) have reported that most Ra-226 in phosphogypsum is associated with fine phosphogypsum grains. The fact that Ra-226 is more closely associated with the finer hemihydrate particles than the larger dihydrate particles is the basis of procedures designed to lower the radioactivity of phosphogypsum (Palmer and Gaynor, 1984; Moisset, 1990).

It has been known for a long time that Ra and Ba co-precipitate together as sulfates (Doerner and Hoskins, 1924). The solubility product constants (25°C) for radium sulfate and barium sulfate are $10^{-10.4}$ and 10^{-10} , respectively (Sillen and Martell, 1964; Gilkeson et al., 1983). The ionic radius of Ra^{2+} is 0.152 nm, while that for Ba^{2+} is 0.143 nm (Ames and Rai, 1978). In phosphogypsum, high Ca and low pH probably result in the solubility of solid solutions dominating the pore water chemistry of Ra because adsorption is negligible under these conditions (Langmuir and Melchoir, 1985). There is evidence that nucleation of Ra sulfate may be inhibited if Ba is not present (Gilkeson et al., 1983 cited by Upchurch et al., 1991). Moisset (1980, 1988, 1990) reported that Ca, Sr, and Ba co-precipitate into small spheres which exist individually or attached to the surface of calcium sulfate crystals. Langmuir and Melchoir (1985) found brines undersaturated by 5–6 orders of

magnitude with respect to pure RaSO_4 . The Ra-226 concentration in the brine was probably controlled by the solubility of Ra in trace solid solutions with Sr and Ba. Sebesta et al. (1981) determined the predominant particulate form of Ra and Ba in uranium waste waters to be Ba(Ra)SO_4 .

Not all Ra-226 in phosphogypsum originates from precipitation of sulfate compounds during

the wet phosphoric process. Some Ra-226 in phosphogypsum may also originate from phosphate rock particles which have survived the sulfuric acid attack.

Even though Ra is considered to be relatively immobile there are some instances where high levels have been found in groundwater systems (SENEC, 1987). Radium may form a soluble sulfate species such as the neutral RaSO_4^0 ion pair

Table 6

U.S. Drinking Water Regulations and Canadian, European Economic Community (EEC) and World Health Organization (WHO) Guidelines^a

Substance	U.S. maximum contaminant level ^b (mg l ⁻¹)	Canadian maximum acceptance limit ^c (mg l ⁻¹)	EEC maximum admissible concentration ^c (mg l ⁻¹)	WHO Guideline Value ^c (mg l ⁻¹)
Inorganics				
As	0.05	0.05	0.05	0.05
Ba	1.0	1.0	0.1	NS
Cd	0.01	0.005	0.005	0.005
Cr	0.05	0.05	0.05	0.05
Fluoride	4.0	1.5	NS	1.5
Pb	0.05	0.05	0.05	0.05
Hg	0.002	0.001	0.001	0.001
Nitrate-N	10.0	10.0	50	10
Se	0.01	0.01	0.01	0.01
Ag	0.05	0.05	0.01	NS
Radionuclides				
Beta particle and photon activity	4 mrem	NS ^c	NS	1 Bq l ⁻¹
Gross alpha activity	15 pCi l ⁻¹ (0.56 Bq l ⁻¹)	NS	NS	0.1 Bq l ⁻¹
Ra-226 + Ra-228	5 pCi l ⁻¹ (0.19 Bq l ⁻¹)	1 Bq l ⁻¹ (Ra-226 only)	NS	NS
Other				
Chloride	250	250	25 ^d	250
Cu	1	1.0	variable ^d	1.0
Fe	0.3	0.3	300	0.3
Mn	0.05	0.05	50	0.1
Sulfate	250	500	25 ^d	400
Zn	5	5	variable ^d	5.0
pH	6.5–8.5	6.5–8.5	6.5–8.5 ^d	6.5–8.5
TDS ^f	500	500	NS	1000

^aThis table is only a partial list of drinking water regulations and guidelines adapted from van der Leedon et al. (1990).

^bU.S. Inorganic and Radionuclide Categories are enforceable; Others are non-enforceable.

^cNon-enforceable.

^dGuide level since no maximum admissible concentration.

^eNo standard.

^fTDS = total dissolved solids.

(Upchurch et al., 1991). However, of the alkaline earth metals Ra shows the least tendency to form complexes (Ames and Rai, 1978). Until water becomes saturated with RaSO_4 and precipitation occurs, RaSO_4° complexes may be a major means of transport in groundwater systems (Upchurch et al., 1991).

Radium exists only as a divalent cation and is not directly affected by redox reactions; however, bacterially mediated redox reactions can indirectly solubilize heavy metals and radionuclides such as Ra-226 from (Ba, Ra) sulfate sludges. Thus anaerobic conditions may greatly increase the mobility of Ra-226 in the environment. Fedorak et al. (1986) studied the effect of sulfate reducing bacteria on release of Ra-226 from (Ba, Ra) SO_4 uranium mine sludges. They found approximately 400 Bq l^{-1} of dissolved Ra-226 in anaerobic uranium mine waste during laboratory batch incubations when high levels of lactate were added to the samples. The fact that Ra-226 release was increased by three orders of magnitude after carbon supplementation was considered to be of great practical significance (Huck and John, 1989). The U.S. drinking water standard for Ra-226 plus Ra-228 is 0.19 Bq l^{-1} . The Canadian drinking water guideline for Ra-226 is 1 Bq l^{-1} (Table 6).

The geochemical nature of groundwater influences Ra-226 concentrations. The leachability and retention of Ra-226 in groundwater may be enhanced by a solution of high ionic strength, such as groundwater with high total dissolved solids (Kaufman and Bliss, 1977; Burnett et al., 1988). Under these conditions high concentrations of other ions may out-compete Ra-226 for adsorption sites, thereby allowing more Ra to remain in solution.

Radon. There are 27 known isotopes of Rn gas, but only Rn-222 is produced in significant amounts by phosphogypsum made from sedimentary phosphorites. Radon-222 forms from the alpha decay of Ra-226. The radioactive gas has a relatively short half-life, 3.82 days, and forms Po-218 by alpha decay. Radon-222 is an inert, noble gas which is an environmental concern because it can be highly mobile and eventually decays to form two relatively long-lived radioactive daughters, Pb-210 and Po-210. The gas is soluble in

water (partition coefficient = 0.35; Conc. in water/conc. in air at 10°C), and solubility increases with decreases in temperature. Solubility in organic liquids may be several orders of magnitude greater than in water (Cothorn, 1987).

Not all the Rn-222 atoms formed from Ra-226 decay are released from mineral structures. Emanation is the process whereby Rn is released from the crystal structure. The emanation coefficient is the number of Rn-222 atoms which escape from the solid phase divided by the total number of Rn-222 atoms which form from the decay of Ra-226. Emanation coefficients for Rn-222 in crystals of apatite, monazite and uraninite have been measured to range between 0.5% and 25% (Rama and Moore, 1984). Phosphogypsum typically has an emanation coefficient of approximately 15% (Roessler et al., 1979b; Pensko et al., 1980; Ackers et al., 1985). Once Rn-222 has been released from the crystal structure it is free to diffuse through the pore spaces of the Ra-226 bearing material and reach the atmosphere. The exhalation rate is the flux density of Rn-222 gas entering the atmosphere from the surface of a Ra-226 bearing material ($\text{Bq m}^{-2} \text{ s}^{-1}$) (SENES, 1987). The factors which determine the exhalation rate of Rn-222 from a source such as phosphogypsum are the Ra-226 content and its distribution, the emanation coefficient, atmospheric pressure, and the diffusion coefficient for radon. The diffusion coefficient will vary greatly depending on temperature and moisture levels (Windham and Horton, 1980). Cracks and crusts on the surface of phosphogypsum will greatly influence exhalation rates.

As Ra-226 forms Rn-222 a high speed alpha particle is ejected from the nucleus, carrying most of the excess energy produced during the radioactive decay. The newly formed Rn-222 atom recoils in the opposite direction with a kinetic energy which is 104–105 times greater than typical bond energies (Michel, 1987). As a result, the recoiled Rn-222 atom can move within mineral structure up to a distance of 70 nm (Tanner, 1964, 1980). If the mineral surface is present within this distance the Rn-222 atom may escape the crystal and be free to enter pore air or pore water. Thus, the amount of Rn-222 which is potentially available for release from a mineral is in part related to the

surface area to mass ratio (Michel, 1987; Burnett et al., 1988). The energy of recoiling atoms is sufficiently high that some atoms cross intraparticle pore spaces and become embedded in adjacent crystal structures. Water in intraparticle pores reduces the energy of the ejected atoms, decreasing the proportion which are re-embedded in other mineral structures. Thus, water may increase the emanation coefficient. High moisture contents may decrease Rn-222 transport to the atmosphere because the gas has a relatively short half-life, and because diffusion of Rn-222 in water is several orders less than in air. Transport of Rn-222 in solution may be substantial if water is rapidly flowing through the mineral matrix in which Rn is emanating. Some Rn-222 progeny are relatively long-lived and may be transported long distances in water (Upchurch et al., 1991).

Thorium. Thorium radionuclides occur in the +4 oxidation state and form sparingly soluble compounds with hydroxides, fluoride and phosphate. Compounds of chloride, nitrate and sulfate are relatively soluble. Complexes with fluoride, chloride, nitrate, phosphate and sulfate dominate its solution chemistry. Total Th in solution decreases as pH is increased to 5. At >pH 5 further pH changes have little effect on Th concentration in solution due to the formation of $\text{Th}(\text{OH})_4^0$. Thorium readily hydrolyzes in acidic environments. Adsorption of Th to surfaces increases with pH and decreases in soil particle size. The element has been reported to migrate mainly in polymeric colloidal form (Ames and Rai, 1978). Th-228 and Thorium-230 are more commonly found in groundwaters than is Th-232. Thorium isotopes from the U-235 decay series are not very prevalent due to the scarcity of the U-235 parent (Osmond et al., 1985).

Lead. Most Pb-210 will be partitioned into the phosphoric acid during the wet phosphoric acid process. The activity of Pb-210 in phosphogypsum will therefore be determined by the ingrowth of Rn-222 and its 3.82 day half-life. In the U-238 decay series Pb-210 is the first decay product after Rn-222 which has a half-life of any significant length (21 years). Lead-210 decays via beta-decay and is not as much of a health risk as the alpha producing radionuclides, but its long half-life

assures that it will exist for long periods of time. Also significant is the fact that it decays to eventually form Po-210, which is a relatively long-lived alpha emitter (138 days). The rate of ingrowth of subsequent decay products is determined by the half-life of Pb-210. Lead speciation and solubility are controlled by Eh and pH. The element exists in the +2 and +4 oxidation states but the +2 state usually dominates. Solubility is low (2 mg l^{-1}) except in acidic environments (Upchurch et al., 1991). Lead carbonate and PbSO_4 are quite insoluble and often control the solubility of lead in oxidizing environments. Under reduced conditions Pb is likely to precipitate as PbS. Adsorption onto clays and organic materials may keep solution concentrations low.

Polonium. Most Po-210 is partitioned into the phosphogypsum during wet phosphoric acid production. Polonium-210 has been found to be abundant in groundwater aquifers below mined lands in Florida where it constitutes most of the gross alpha activity. This radionuclide exists in several valence states with the +4 being the most common. However, the chemistry of Po is not clearly understood (Upchurch et al., 1991). Polonium mobility is controlled by the solubility of the radiocolloids formed by complexing of the element with hydroxyl. Polonium is most mobile in acidic systems. Under alkaline systems it forms a polonium-hydroxyl radiocolloid, often coprecipitated with iron-hydroxyl colloids, which are not very mobile (Upchurch et al., 1991). Complexes between Po and organic compounds may also be important in Po mobilization (Oural et al., 1989). Upchurch et al. (1991) state that there is little direct evidence that ion exchange or redox reactions play a large role in Po mobilization. However, they do note that Po solubility may be influenced by redox reactions of S. Polonium solubility is high in reducing, sulfide rich waters. Particulate Po increases as sulfide is oxidized (Harada et al., 1989). If redox conditions and soluble organic matter levels are suitable for sulfate reduction it is likely that Po-210 will become mobile if pH is not too high.

3.4. Studies of solubility-controlling solids

There have not been very many studies which

have examined the factors which control the mobilization of trace elements and radionuclides in phosphogypsum. Most chemical studies have focused on the elemental composition of the material, or have been empirical leaching studies. Mattigod et al. (1990) and Eary et al. (1990) proposed that these types of studies should be complemented with studies which examine the thermodynamics of specific dissolution/precipitation, adsorption/desorption, and speciation reactions which occur during the weathering of industrial by-products. This latter approach permits predictions of leachate behavior under a wide range of conditions which are not possible with empirical leaching studies. If solubility-controlling solids of an element are present in a waste, or may precipitate from it, then the long-term aqueous concentrations can be predicted from thermodynamic data and adsorption/desorption reactions may be ignored (Eary et al., 1990). Even though thermodynamic data are available for pure-phase secondary solids containing trace elements, there is a lack of data for solid solutions, especially those for radionuclides. If conditions for solubility-controlling solids are not present, or if kinetics are too slow, then dissolution rates and/or adsorption reactions will dominate (Eary et al., 1990). In nature non-equilibria may occur as a result of slow kinetics or microbial catalysis. Changes in the oxidation state of some elements will also influence the above processes. Acidic, aerobic conditions would be expected to define the pore water chemistry of phosphogypsum, however reduced conditions may develop near the base of a stack. The pH of phosphogypsum may approach neutrality as the material ages.

The application of chemical speciation to predict the mobility of trace elements in phosphogypsum and phosphogypsum process water is lacking. Of the little speciation data which has been published, most has been for the major rather than for the minor elements. Murray and Lewis (1985) used GEOCHEM to predict the fate of fluoride, orthophosphate and sulfate from phosphogypsum leachate as it reacted with simulated soil systems. Their results will be elaborated in a later section. Lewis (1988) extended this work further by examining the fate of Ra-226 species originating

from uranium mill waste solutions in simulated soil systems using GEOCHEM. The simulated and experimental results did not match very closely. The inconsistency was explained by Lewis (1988) as being the result of a poor data base for Ra-226 species, particularly for mixed-solid species. Radium is known to form solid solutions with some elements such as Ba and Sr (Langmuir and Melchior, 1985); however, thermodynamic data for Ra solid solutions are not complete.

May and Sweeney (1984b) evaporated the leachate water from phosphogypsum but X-ray diffraction of the evaporite did not help to identify any trace element compounds. Literature studies of phase equilibria in saturated gypsum solutions were used to identify possible trace element compounds. The expected specific compounds of trace elements were sulfates, except for the Ca compounds of arsenate, chromate and selenate.

Luther and Dudas (1993) examined solution extracts from 80-day batch incubation studies of phosphogypsum, phosphogypsum-soil mixtures and soil alone. Speciation of major and trace elements was performed using GEOCHEM. As pH was raised due to soil addition most free cations decreased, OH^- interactions increased and PO_4^{3-} and SO_4^{2-} interactions decreased. Concentrations of Cd, Fe, Ni, P, Sr, V, and Zn in solution decreased by close to an order of magnitude. Soil addition increased Ca^{2+} and Cd^{2+} interactions with SO_4^{2-} . AsO_4^{3-} , CO_3^{2-} , PO_4^{3-} and SeO_3^{2-} were mainly combined with H^+ in phosphogypsum leachate and the proportion decreased with neutralization. Nitrate, SO_4^{2-} and SeO_4^{2-} existed mainly in the free state and this fraction increased with neutralization.

Luther and Dudas (1993) also compared ion activities predicted by GEOCHEM with theoretical levels using solubility constants for potential solubility-controlling solids of Al, As, Ca, Cd, Cu, Fe, P, S, Se, Si and Zn. Aluminum activities were consistent with the presence of the solubility-controlling solids of alunite, basaluminite, gibbsite and jurbanite. Under acidic conditions and high sulfate levels the aluminosulfate minerals alunite and basaluminite were predicted to be the most stable (O'Brien and Sumner, 1988; Alva et al., 1991).

Solubility-controlling solids for the trace ele-

ments could not be identified by Luther and Dudas (1993) because solutions were undersaturated relative to the potential minerals for which thermodynamic data were available. Thus the effects of precipitation/dissolution and adsorption/desorption could not be resolved. Spiking the material with trace elements might allow for the prediction of solubility-controlling solids if they existed (Rai and Szelmeczka, 1990). The batch incubations showed that Cd concentrations were high in phosphogypsum pore water but concentrations of this element, along with Cu and Zn, decreased greatly with increases in pH. Arsenic and Se concentrations did not decrease greatly with pH increases and, along with SO_4^{2-} and F^- , were identified as potentially posing an environmental risk if leached downwards into groundwater systems.

4. Environmental concerns related to the storage of phosphogypsum

Most of the phosphogypsum produced is stored in stacks (Carmichael, 1988). A recent final ruling by the U.S. E.P.A. requires that all phosphogypsum be placed in stacks or mines (Federal Register, 1990). Environmental contamination resulting from phosphogypsum storage may occur from: (i) atmospheric contamination with fluoride or other toxic elements; (ii) groundwater pollution with mobile anions, acidity, trace elements or radionuclides; (iii) radon gas; (iv) inhalation of radioactive dust; and (v) direct exposure of gamma radiation. Other concerns with storage include surface runoff (Rydzyński, 1990), and erosion and stability of the stacks. Several authors have published methods of reducing fluoride, radionuclides and heavy metals in phosphogypsum by treatments before, during or after the wet phosphoric acid process (Becker, 1989; Jdid et al., 1986; Kazak et al., 1988; van der Sluis et al., 1988; Habashi, 1989; Moisset, 1990). Mitigation and closure of phosphogypsum storage sites are discussed by Berish (1990) and Norlander (1988).

4.1. Atmospheric fluoride

Fluoride gas emission is only a concern with operational stacks; however, transport of fine dust

particles containing F^- is a potential problem for both operational and inactive stacks. Phosphate rock may contain 4% fluorine which forms HF during the acidulation process. Fluoride remains in the liquid phase but during processing gaseous SiF_4 and gaseous HF may be formed under high temperature conditions. When phosphogypsum is sluiced to the stack some gaseous F^- may be evolved; however, most plants use scrubbers to remove F^- .

Linero and Baker (1978) evaluated previous F^- emission rate studies to determine a F^- emission factor which could be used for predictive modelling. None of these studies were ideal, however it was concluded that the characteristic emission factor for cooling ponds fell in the range of 0.1–10 lb acre⁻¹ day⁻¹ (30–3400 $\mu\text{g cm}^{-2}$ 30 days⁻¹). Modelling predicted that ambient F^- concentrations near a typical pond would be sufficiently high to require technologies to control F^- emission.

SENES (1987) discussed the F^- monitoring programs in place at two sites in Canada. The Ontario site was the focus of two phytotoxicological surveys. The results of this monitoring showed that probably only operating facilities result in elevated ambient F^- levels. The Ontario Ministry of the Environment (OME) established 35 $\mu\text{g g}^{-1}$ as the upper limit of normal background concentration of F^- in foliage. During plant operation foliage samples exceeded this level as far away as 6 km from the plant site (McLaughlin, 1986). Wild grape, a plant very sensitive to F^- , showed damage in the areas surrounding the plant site.

Fluoridation rates in the area surrounding the Ontario site were measured by the OME. Annual averages ranged from 18 $\mu\text{g F}^-$ 100 cm⁻² 30 days⁻¹ at a station 5.4 km away to as high as 927 $\mu\text{g F}^-$ 100 cm⁻² 30 days⁻¹ at a station close to the operating site. Seasonal variation of ambient fluoridation levels was observed to be greatest in the summer. Fluoridation rates declined greatly when operation of the phosphoric acid plant ceased (SENES, 1987).

Ambient fluoridation levels were also measured immediately adjacent to the ponds and plant at an operating site in Calgary, Alberta. Seasonal and spatial variation was observed with rates ranging

from a low of $6 \mu\text{g F } 100 \text{ cm}^{-2} \text{ 30 days}^{-1}$ to a high of $5170 \mu\text{g F } 100 \text{ cm}^{-2} \text{ 30 days}^{-1}$. Maximum air quality guidelines for fluoridation levels are $40 \mu\text{g } 100 \text{ cm}^{-2} \text{ 30 days}^{-1}$ in Alberta, and 80 and $40 \mu\text{g F } 100 \text{ cm}^{-2} \text{ 30 days}^{-1}$ in Ontario for growing and non-growing seasons, respectively.

4.2. Groundwater pollution

Groundwater contamination may occur from process water seepage during operation of a stack or through the long-term downward leaching

which occurs when rainwater infiltrates through an inactive stack.

Several studies have investigated groundwater pollution or the potential leachability of phosphogypsum constituents. The results are not consistent although it is clear that the potential for groundwater pollution under a phosphogypsum stack is a concern in some situations.

Acidic seepage waters may be buffered by alkaline subsoils and groundwaters, thereby reducing the mobility of certain heavy metals (e.g. Ni, Co,

Table 7

Reported values for chemical composition of phosphogypsum process water (units are mg l^{-1} unless otherwise stated)

Parameter	Source	Miller and Sutcliffe Jr. (1982)		Murray and Lewis (1985)	Rouis and Bensalah (1990)
		Becker (1989)	AMAX ^a USSAC ^b		
Al	160 (64–210) ^c		400	100–500	0.41
As		0.92	0.63		
B		3.0	2.7		
Ba		0.50	0.50		
Ca	1430 (350–3360) ^c	30	30	350–1200	1654
Cd		0.51			0.62
Cl		15		200	1520
Co		0.17	0.5		0.18
Cr		0.68	3		2.7
Cu		0.21	0.5		0.08
F	10 000 (900–12 000)	4300	7700	3000–10 000	5539
Fe	105 (77–770) ^c	63	41	70–300	12.8
Hg		$0.2 \mu\text{g l}^{-1}$	$0.2 \mu\text{g l}^{-1}$		0.6
K	208 (10–370) ^c	220	110		62
Mg	240 (36–350) ^c	120	52	240	182
Mn		6.1	130	8	
N ^f		1780	142		
Na	1480 (280–2000) ^c	2200	790	1600	2556
Ni		1.5	0.42		
P ₂ O ₅		9850 ^c	21 000 ^c	6000–12 000	4015
Pb		0.08	0.11		0.18
SiO ₂		2800	3000	2000–4000	2018
SO ₄	4800 (2800–10800) ^d	4700	5000		5385
Sr		0.41	0.92		28
Ti					0.42
Zn		2.7	3.7	1.0–1.8	4.0
pH	1.5 (1.2–2.5)	1.8	1.3		1.8

^aCooling water (Sample S2) at AMAX Phosphate Inc., central Florida.

^bCooling water from return ditch (Sample S2) at USS Agri-Chemicals plant, central Florida.

^cConverted from oxide values.

^dConverted to SO₄ from reported SO₃.

^eConverted to oxide from total P.

^fOrganic N plus ammonium N.

Cu) (SENES, 1987). However, other chemical species such as SO_4^{2-} and F^- are not affected as much by pH changes from the stack to the subsoil. Site specific conditions which may mitigate the impact of possible contaminants on groundwater are: (i) suitable subsurface geology which can neutralize acidic seepage; (ii) construction of the stack on an impervious layer; and (iii) construction

of interceptor wells or ditches. Other sources have reported methods of reducing seepage of contaminants from active and inactive stacks (Gipson, 1985; Wissa, and Fuleihan, 1980; Wrench and Smith, 1986; Kleinschmidt, 1990; Rouis and Bensalah, 1990).

Process water. The recycled process water used to sluice phosphogypsum out to the stacks is aci-

Table 8
Reported radionuclide activities (Bq l^{-1}) in phosphogypsum process water

Isotope	Activity ^a	Site description	Reference
Ra-226	1.9	AMAX ^b	Miller and Sutcliffe Jr., 1982
	3.2	USSAC ^c	
	2.6	Plant A	Guimond and Windham, 1975
	3.2	Plant B	
	2.0	Plant C	
U-234	70	AMAX	Miller and Sutcliffe Jr., 1982
	140	USSAC	
	28	Plant A	Guimond and Windham, 1975
	65	Plant B	
	25	Plant C	
U-235	2.5	AMAX	Miller and Sutcliffe Jr., 1982
	8.1	USSAC	
	1.3	Plant A	Guimond and Windham, 1975
	3.7	Plant B	
	1.3	Plant C	
U-238	72	AMAX	Miller and Sutcliffe Jr., 1982
	120	USSAC	
	27	Plant A	Guimond and Windham, 1975
	68	Plant B	
	25	Plant C	
Th-227	0.3	AMAX	Miller and Sutcliffe Jr., 1982
	2.3	USSAC	
Th-228	0.67	AMAX	Guimond and Windham, 1975
	0.63	USSAC	
	0.11	Plant A	
	0.15	Plant B	
	0.03	Plant C	
Th-230	4.2	AMAX	Miller and Sutcliffe Jr., 1982
	69	USSAC	
	3.2	Plant A	Guimond and Windham, 1975
	15	Plant B	
	0.3	Plant C	
Th-232	0.52	AMAX	Miller and Sutcliffe Jr., 1982
	0.89	USSAC	
	0.14	Plant A	Guimond and Windham, 1975
	0.23	Plant B	
	0.15	Plant C	

^aDissolved plus suspended activities.

^bCooling water, Sample S2 at AMAX Phosphate Inc.

^cCooling water from return ditch, (Sample S2) at USS Agri-Chemicals Plant.

dic. Sulfuric, phosphoric and fluoridic acids reside in the phosphogypsum pores after acidulation and filtration. Consequently, elements solubilized from phosphate rock during the acidulation process may remain in solution. This process water is present in cooling ponds and also within the porosity of the phosphogypsum stack.

The species solubilized during acidulation include As, Cd, Cr, Pb, Na, F^- , Mn, Fe, SO_4^{2-} , U and Th (Roessler, 1979a; Berish, 1990). In addition to toxic elements, the process water contains high levels of total dissolved solids (Rea and Woods, 1985). Elemental composition of process waters is reported in Tables 7 and 8. The waters do not meet many of the limits set for drinking water regulations and guidelines (Table 6).

Laboratory studies. Murray and Lewis (1985) determined the extent to which natural geological materials could remove fluoride, sulfate and orthophosphate from phosphogypsum leachate under laboratory conditions using graded, serial batch leaching systems. The minerals investigated were sand, Ca-montmorillonite, kaolinite, calcium carbonate and iron (III) hydroxide. The chemical equilibrium model GEOCHEM was used to speciate the leachate solutions. Calcium carbonate removed large proportions of F^- and orthophosphate and smaller proportions of sulfate by precipitation as CaF_2 , calcium phosphate and/or calcium fluorophosphate and $CaSO_4$. Sufficient calcium carbonate was needed to maintain a high solution pH, otherwise redissolution of F and orthophosphate occurred. Sand only removed small quantities of F^- , probably by anion adsorption. Both kaolinite and montmorillonite removed large quantities of soluble F and orthophosphate from solution. The removal increased with increasing pH, likely due to a combination of complex formation, the degree of phosphate ionization and changes in clay charge characteristics. The removal of F^- by kaolinite was probably due to positive charge development on the clay. At pH 4, 84% of F existed as free F^- and the AlF_4^- complex. Iron(III) hydroxide had little effect on F^- or orthophosphate removal when mixed with clays but markedly increased SO_4^{2-} removal when Ca was abundant, probably by the formation of Ca phosphate complexes which reduce competi-

tion with sulfate for adsorption on clays or Fe (III) hydroxide. According to Murray and Lewis (1985) calcareous strata below phosphogypsum may be very effective in precipitating F^- and orthophosphate.

May and Sweeney (1984b) evaluated the leachability of Ra and elements the E.P.A. has classified as toxic by using the standard E.P.A. 'EP' extraction procedure (Federal Register, 1980). Additional elements (Cu, Ni, K and Na) were included in the analysis. The concentrations of toxic elements in the extract were all below E.P.A. maximal concentrations, therefore the material was considered non-toxic by E.P.A. standards. The authors estimated that the inclusion of Ra into the phosphogypsum crystal structure would be 89% of the amount originally present, indicating that very little Ra would be leached. May and Sweeney (1984b) estimated the Ra to move at approximately 1/200 the seepage rate.

SENES (1987) conducted leachate studies on two composite phosphogypsum samples taken from sites located at Dunnville, Ontario and Calgary, Alberta. The Ontario material was from an inactive stack while the Alberta material was taken from an active stack. The leachate test involved agitating the solid in distilled water (1:10 ratio) for 24 h followed by filtering. All measured concentrations of toxic elements were below the E.P.A. criteria, although the Cd and Cr concentrations from the Alberta site were much greater than values found at the Ontario site or by May and Sweeney (1984a) in Florida phosphogypsum. The Alberta phosphogypsum was acidic due to the presence of residual process water. Relatively high concentrations of Al, Cd, Cr, Fe, Mg, Ni and V were attributed to the low pH and relatively high solubility of the metallic hydroxides (SENES, 1987). The leachate from the Ontario phosphogypsum had a pH of 6.02. Although it contained elevated levels of Ca, SO_4^{2-} , P, F^- , and Al, they were lower than those from the Alberta material. Heavy metal concentrations were much lower than in the Alberta phosphogypsum leachate. According to SENES (1987), the results showed that leachate from fresh phosphogypsum exceeded both mining discharge objectives and Canadian drinking water standards. Aged phosphogypsum

may meet mining discharge objectives except for P, Al and possibly Cd. Fluoride and SO_4^{2-} levels are likely to be exceeded even in aged phosphogypsum material (SENES, 1987). Lead-210, a relatively long-lived radioactive product from the U-238 decay chain, was 100-fold greater in the Alberta phosphogypsum leachate than in the Ontario phosphogypsum leachate and exceeded the World Health Organization Guideline for beta particle activity (1.0 Bq l^{-1}) by three times.

Naff (1984) conducted a leachate study to determine the potential environmental impact of phosphogypsum from Mobil Chemical Corporation. Fresh, aged and stabilized phosphogypsums were analyzed using the standard E.P.A. EP extraction procedure. The results were within the permissible E.P.A. limits for toxicity, however SO_4^{2-} and fluoride levels exceeded drinking water standards.

Luther et al. (1993) determined the equilibrium concentrations of major and trace elements in phosphogypsum pore water taken from an inactive phosphate plant in southern Alberta in order to evaluate the groundwater contamination potential of phosphogypsum. Some extracts had higher levels of As and Cr than those found by May and Sweeney (1984b), but all pore water samples were more concentrated in Cd and Se. Luther et al. (1993) determined that all extract samples exceeded Canadian drinking water guidelines (CDWG) for Cd, Se, SO_4^{2-} and total dissolved solids. Some samples exceeded CDWG for As, Cd, Cr, Cu, Fe, Mn, Na, $\text{NO}_3\text{-N}$ and Zn (Table 6). The pH of the pore water extract was 3.4, which is below CDWG. Fluoride levels were not measured by Luther et al. (1993); however, Roberts-Thorne (1990) determined levels to be $26 \mu\text{g g}^{-1}$ at the same site a few years earlier. Canadian DWG requires fluoride to be $<1.5 \mu\text{g g}^{-1}$ (Health and Welfare Canada, 1993).

Field studies. SENES (1987) summarized work by Miller and Sutcliffe (1982) for two operational stacks in central Florida (AMAX Phosphate Inc. and USS Agric-Chemicals Ltd.) which are located on limestone bedrock that is overlain by phosphatic clay deposits and a surficial sand layer. Groundwater in the area is characterized by hard, calcium magnesium bicarbonate water with low SO_4^{2-} and Cl^- concentrations. Both stacks caused

slight distortions in the groundwater level which reflected recharge of water from the stack and pond areas. Significant degradation in groundwater quality was detected at the two sites. Many chemical parameters showed levels up to several orders of magnitude greater than natural groundwater concentrations. Relative to background concentrations, the groundwater below the two sites showed elevated concentrations of Si, Na, SO_4^{2-} , F^- , hardness, P and N. Concentrations of Cu, Mo and Zn were also elevated. Low pH was also found near the gypsum stacks and cooling ponds at the USS site. Movement of contaminants in a plume was observed at both Florida sites. Groundwater 600 m from the USS stack showed sulfate concentrations which were 450 times greater than background levels. Groundwater 460 m from the AMAX stack had sulfate concentrations up to 1900 mg l^{-1} (SENES, 1987). Selected members from the U-238, U-235 and Th-232 decay chains were also measured in the groundwater below the AMAX site. Radium-226 was measured below the USS site. All radionuclides, except for Ra-226 at the USS site, were within drinking water standards, however U-238 was elevated over background in some samples. At both sites elevated levels of Ra-226 were observed hundreds of meters from the stacks, indicating Ra-226 migration through the groundwater systems (SENES, 1987).

SENES (1987) reviewed groundwater studies which have been conducted near phosphogypsum stacks in Alberta at sites operated by three fertilizer manufacturers. All sites are located on relatively flat terrain underlain by glacial till. Near surface groundwater quality is poor so drinking water and irrigation water is obtained from deep groundwater or surface water. It was not possible to compare groundwater quality between sites because different monitoring criteria were used at each site. The criteria set for background levels were conservative and were based on taking the lowest values observed in observation wells to represent background levels. Sulfate concentrations were found to be much greater than apparent background. Fluoride concentrations of up to 32 mg l^{-1} were detected, which are several orders of magnitude greater than background. SENES

(1987) did not think that heavy metals would be very mobile in these groundwater systems because pH values ranged between 6.5 and 8.7. Levels of Ca, P and N species were elevated above background in some wells.

May and Sweeney (1984b) supplemented their laboratory studies (see above) of the leaching characteristics of phosphogypsum stockpiles by detailed sampling through a short section both above and below the ground:phosphogypsum interface. Subsurface analysis was not available prior to phosphogypsum stacking and was estimated using averages from similar geological materials. It was concluded that Ra-226 and metallic elements were not leached from the phosphogypsum stockpiles.

Toxicity analysis of phosphogypsum was conducted by May and Sweeney (1982, 1984a, 1984b) on nine Florida stacks in order to assess the potential environmental impact of the material. Both active and inactive stacks were included in the study. Part of the study involved measuring the total elemental composition throughout the stack profile. The researchers hypothesized that if significant leaching of elements occurred, there would be a non-uniform distribution of elements down through the stack. They concluded that significant leaching had not occurred because a uniform distribution of elements was found.

Berish (1990) summarized a groundwater study conducted in Florida by Bromwell and Carrier (1987). Data from surficial groundwater at four phosphogypsum sites in Florida were used to calculate distances downstream from a theoretical phosphogypsum site at which contaminant concentrations would not exceed E.P.A. Drinking Water Standards. Concentrations of Se, Ag and F^- were attenuated quickly and were below the E.P.A. maximum contaminant levels for Primary Drinking Water Standards within 100 feet of the source. Lead and As concentrations met these standards within 300 feet and 800 feet, respectively. Cadmium and Cr were more mobile and were not attenuated until up to 1200 feet from the source. Iron, SO_4^{2-} , Mn and total dissolved solids were very mobile but limited data made it difficult to make an accurate estimation of the size of the impact zone. However, it was estimated that the

non-exceedance zone would be greater than 610 m from the source and would be highly dependent on site specific geologic and hydrologic conditions. Shallow surficial aquifers were the main groundwater systems contaminated by phosphogypsum stacks.

Rouis and Bensalah (1990) investigated the groundwater contamination below a phosphogypsum stack in Tunisia. The pH of the groundwater near the stack was less than 2. It was neutral 200 meters downstream from the stack. Phosphate and F^- levels near the stack were as high as 16300 and 8800 $mg\ l^{-1}$, respectively. Mercury and Mo levels were as high as 0.60 and 0.19 $mg\ l^{-1}$, respectively. The region of high groundwater contamination extended 100 to 400 meters downstream from the phosphogypsum stack.

Other studies have investigated the groundwater pollution potential of phosphogypsum which has been used as a base for road construction (Chang et al., 1989; Bandyopadhyay et al., 1990; Nifong, 1990). These studies reported no adverse effects of phosphogypsum on groundwater quality.

4.3. Radon gas and other radioactive exposure

Roessler (1986) summarized the pathways of radioactive exposure originating from phosphogypsum to humans. Exposure to Rn-222 gas is one of the greatest health concerns. This section will review the studies which have investigated the magnitude of Rn-222 gas evolution and the significance of these rates. Other forms of aerial exposure, such as radioactive dust particles and direct gamma radiation from phosphogypsum stacks, will also be included in this section. Before discussing Rn-222 it is appropriate to summarize simple dosimetry, the means by which radioactive exposure is measured. A more comprehensive description of the subject is offered by references such as Cothorn (1987) or Lao (1990).

Several terms are used to describe the health effects of radionuclides such as Rn-222 and its progeny. The working level (WL) has been in use since 1955 and describes the potential alpha energy concentration of radon progeny. A WL is defined as the exposure rate of 1.3×10^5 MeV (2.08×10^{-5} J) of potential alpha energy/liter of air. This is the energy released from the total decay of short-

lived Rn-222 progeny to Po-214 in radioactive equilibrium with 3700 Bq m^{-3} (100 pCi l^{-1}) of Rn-222. The working level month (WLM) corresponds to an exposure of 1 WL during 1 month (approx. 170 h). In terms of radon progeny concentration, a WL of 0.001 is representative of average outdoor concentrations. Average indoor levels are 0.004 WL. The level recommended for remedial action by the U.S. National Council on Radiation Protection and Measurements (NCRP, 1984) is 0.04 WL. Assuming 0.5% equilibrium between radon and its progeny, this is equivalent to a radon concentration of 300 Bq m^{-3} (8 pCi l^{-1}). This results in a continuous exposure rate of about 2 WLM/year (Mills and Egan Jr., 1987). In Canada, remedial measures are recommended when average indoor Rn-222 daughter concentrations exceed 0.02 WL (NCRP, 1984).

Walsh (1990) provided a theoretical argument that current mining risk coefficients, such as the WL, significantly overestimate environmental radon risk because miners are exposed to a complex atmosphere that contains many substances which may potentially cause cancer. Current lung cancer risk assessments assume that radon progeny alone are responsible for differences between miners and control populations.

The absorbed dose, D , refers to the average density of energy absorbed by a mass of cells. In the SI system the unit is the Gray (Gy), equivalent to J kg^{-1} . The conventional unit for absorbed dose is the radiation absorbed dose (rad), which is equivalent to one hundredth of a Gray.

The dose equivalent, H , is a measure of both the energy absorbed by a mass and the biological impact of the absorbed energy. Measured in Sieverts (Sv), it is the product of the absorbed dose, D , the quality factor, Q , and a factor, N (usually 1), which incorporates other modifying factors. The conventional unit for H is the radiation equivalent in man (rem), which is equivalent to one hundredth of a Sievert. The quality factor, Q , is small for gamma and X-rays (1), intermediate for neutrons (5), and high for alpha particles and other heavy nuclei (20). Thus for gamma radiation the radiation absorbed dose (rad) is usually the same as the radiation equivalent in man (rem). The dose equivalent of an organ is calculated by

multiplying H by a weighting factor which takes the radiosensitivity of an organ into consideration. The NCRP (1984) recommendation for general public continuous exposure to gamma radiation above background is $1000 \text{ mrem (10 mSv) year}^{-1}$. Typical exposure to background gamma radiation in the U.S. is $0.28 \text{ mSv year}^{-1}$ ($28 \text{ mrem year}^{-1}$). Canadian estimates are 20% lower (NCRP, 1987).

The effective dose equivalent, (H_E), is a measure of the total risk to the individual and is calculated by summing the dose equivalents of all the organs in the body. Both H and H_E are measured in Sv. The annual effective dose equivalent for all sources of natural background radiation is approximately 2 mSv year^{-1} , which is approximately equal to $200 \text{ mrem year}^{-1}$ (UNSCEAR, 1982; Cothorn, 1987).

Field studies. A number of studies have investigated radon exhalation rates, ambient radon levels and other forms of radioactive exposure at phosphogypsum stacks. To put these values in perspective, typical exhalation rates from soil, the largest source of background radon in the environment is approximately $0.5 \text{ Bq m}^{-2} \text{ s}^{-1}$ per Bq Ra-226 g^{-1} soil (NCRP, 1987). The average concentration of Rn-222 in the global atmosphere is about 3.7 Bq m^{-3} , however concentrations may be 10-times higher over some land areas. Typical Rn-222 levels near open ground are about 5 Bq m^{-3} (Eichholz, 1987; Michel, 1987).

Windham and Horton (1980) reported the exhalation rates of Rn-222 from two active phosphogypsum stacks in Polk County, Florida over several weeks. The mean exhalation rate was $1 \text{ Bq m}^{-2} \text{ s}^{-1}$ although measured rates varied by almost two orders of magnitude. Guidry (1990) reported radon flux from a phosphogypsum stack in central Florida to range from $<0.004 \text{ Bq m}^{-2} \text{ s}^{-1}$ over ditches and beaches on the stack to $3.6 \text{ Bq m}^{-2} \text{ s}^{-1}$ near a roadway on top of the stack. A wide range of variation was observed on the stack, likely due to differences in crusting.

NESHAPS (1989) summarized by Berish (1990) reported Rn-222 exhalation rates from active and inactive stacks in Florida. The greatest flux rates were from the top of dry non-crusts stacks which were active. This material averaged about $0.7 \text{ Bq m}^{-2} \text{ s}^{-1}$. In contrast, exhalation rates were less

than $0.04 \text{ Bq m}^{-2} \text{ s}^{-1}$ from cooling ponds and ditches. Flux from the top of an inactive stack only averaged $0.15 \text{ Bq m}^{-2} \text{ s}^{-1}$ but flux from the sides of a different inactive stack was about four times greater. NESHAPS (1989) also estimated total Rn-222 fluxes from many stacks throughout Florida. Flux rates were estimated to range between 0.09 and $0.34 \text{ Bq m}^{-2} \text{ s}^{-1}$. The computer codes AIRDOS-EPA and DARTAB were used to estimate the maximum exposed individual and also the collective risks of the regional population to Rn-222. Meteorological conditions and distance from the stacks were considered. The maximum exposed individuals were estimated to receive doses $< 6 \times 10^{-5}$ WL above the natural background outdoor level. Collective risk assessment estimated that less than one fatal cancer in 20 years would occur due to the presence of phosphogypsum stacks. Based on this work, the U.S. E.P.A. recently adopted an average $0.74 \text{ Bq m}^{-2} \text{ s}^{-1}$ limit on Rn-222 emissions from phosphogypsum stacks (Federal Register, 1989).

Horton et al. (1988) reported Rn-222 concentrations around the perimeter of 5 phosphogypsum stacks 1 m above ground level. Natural background levels, determined at nine locations greater than 8 km from any phosphogypsum stack, averaged 0.0052 Bq l^{-1} . Average concentration at the base of the phosphogypsum stacks was 0.024 Bq l^{-1} . Roessler (1985) reported Rn-222 concentration to range between 0.011 and 0.015 Bq l^{-1} on or close to a phosphogypsum stack. Concentrations decreased to background within 1000 m.

SENES (1987) found Rn-222 exhalation rates from some stacks at Ontario (clay or topsoil covered stacks) and Alberta (active with bare phosphogypsum dikes with water-filled ponds) to range between 0.037 and $1.1 \text{ Bq m}^{-2} \text{ s}^{-1}$. A typical value of $0.37 \text{ Bq m}^{-2} \text{ s}^{-1}$ was incorporated into the air dispersion model ISC-LT (Wackter, 1986) which estimated Rn-222 air concentrations under meteorological conditions representative of the two sites. At Ontario, it was predicted that maximum annual average Rn-222 concentrations 100 m from non-water covered, bare phosphogypsum stacks would be $1.1\text{--}1.9 \text{ Bq m}^{-3}$ ($0.0011\text{--}0.0019 \text{ Bq l}^{-1}$). Concentrations 100 m from water covered stacks would be approximate-

ly 0.19 Bq m^{-3} ($0.00019 \text{ Bq l}^{-1}$). Some measured background levels in the vicinity were higher than this. The results for the Alberta site were similar in that predicted Rn-222 concentrations 100 m from the stacks were indistinguishable from normal background levels. SENES (1987) also measured ambient Rn-222 concentrations 1–1.5 m above stacks covered with clay in Ontario. The average concentration of 0.011 Bq l^{-1} was not statistically different than background levels (0.0074 Bq l^{-1}) for the area. Radon-222 concentration above water ponds at a phosphogypsum stack in southern Alberta averaged 0.024 Bq l^{-1} , which was not statistically different from the natural background level of 0.017 Bq l^{-1} .

Airborne particulate matter originating from phosphogypsum piles by wind erosion or operations on the stack is also a potential source of radioactivity. Wind erosion is usually not a serious problem on stacks because inactive stacks develop a crust while active stacks generally have a high moisture content which reduces blowing particles (Berish, 1990). NESHAPS (1989) found that annual radionuclide transport from a phosphogypsum stack was very low and the associated health risks were much less than those related to Rn-222 emissions. Similar findings were found by Western and SENES (1983). Air samples were taken 0.8 km south of one phosphogypsum pond in southern Alberta and analyzed for U, Th-230, Ra-226, Pb-210 and Po-210. All radionuclides except Ra-226 were within background levels. The annual Ra-226 intake was estimated to be equivalent to $2.5 \mu\text{Sv}$ which is much less than 2 mSv, the typical annual exposure to natural background radioactivity.

Phosphogypsum stacks are a direct source of gamma radiation due Ra-226 and its daughter radionuclides. Horton et al. (1988) reported gamma radiation 1 m above the surface of 5 phosphogypsum stacks. Average gamma exposure was $33 \mu\text{rads h}^{-1}$ ($33 \mu\text{rem h}^{-1}$). Berish (1990) stated that only people spending long periods of time working on the stack, or living immediately adjacent to it, would be subjected to a health risk because irradiation decreases exponentially with distance. Roessler (1986) (see below) did not think this level of gamma exposure posed an environmental health risk.

Laiche and Scott (1991) conducted a study to determine the potential radiological exposure for people working at the Freeport phosphogypsum pile in Louisiana. Gross gamma exposure rates were measured 1 m above the stack surface. Air samples were also obtained from the same location. The measured gross gamma exposure rates averaged $0.368 \mu\text{Sv h}^{-1}$. The corresponding working year exposure would be 0.48–0.68 mSv above background. This level is low because it represents <10% of the annual dose limit for the general public in unrestricted areas (NCRP, 1984). Radon daughter concentrations measured on the stack ranged between 0.0006 and 0.001 WL, while airborne Ra-226 concentrations were indistinguishable from background.

Roessler (1986) conducted a detailed analysis of the radiological hazards associated with phosphogypsum produced from central Florida rock. He used radiological characteristics of phosphogypsum from a number of sources to determine the exposure hazard of the gamma radiation and airborne radioactivity in the immediate vicinity of the phosphogypsum piles. It was determined that individuals working on a phosphogypsum stack for a year (2000 h) would be subjected to a gamma radiation dose equivalent of 60 mrem. The occupational exposure limit is 5000 mrem year⁻¹. Measured radon concentrations were equal to or less than 0.015 Bq l^{-1} which corresponds to <0.004 WL. This level was equivalent to typical Florida indoor radon concentrations and 10-times less than the level set by the NCRP for remedial action.

Guidry (1990) conducted a detailed analysis of the radon emissions and gamma radiation irradiated from a phosphogypsum stack in central Florida. Radon emission data and measurements of airborne Ra-226 in particulate matter were utilized in the ISCLT atmospheric model to estimate the environmental impact of the stack. The receptor sites for the radiological assessment were located at the nearest point of general public access to the facility, approximately 2000 m from the stack, and also at the location of the maximum exposed individual (MEI). Estimated maximum radon daughter levels at the nearest public access point corresponded to 0.000065 WL while the

maximum concentration at the location of the MEI was less than half of this amount. It was estimated that deposition of Ra-226 in particulate matter for 1000 years would increase soil Ra-226 <0.1%.

5. Utilization of phosphogypsum in agriculture

Many studies have reported the effects of applications of phosphogypsum on nutrient levels and the physical and chemical properties of agricultural soils. The benefits of phosphogypsum have been documented as amendments for: (i) highly weathered soils, with relatively low exchange capacities and/or low levels of extractable nutrients; (ii) soils with high sodicity resulting in dense subsoil horizons, and those with variable sodicity at the surface which are prone to dispersion and crusting; (iii) acid soils with high levels of Al; and (iv) calcareous soils. Crop yields and quality of a variety of fruit, vegetable, grain, forage, and oilseeds have generally been found to be higher on phosphogypsum amended soils. The wide scale use of phosphogypsum appears to be restricted until concerns regarding associated natural radionuclides, F⁻, heavy metals, effect on nutrients, potential as a source of P in surface water pollution, and economic considerations are more fully addressed. Despite these environmental concerns regarding phosphogypsum, some countries have made wide-scale use of the by-product as a soil amendment (Beretka, 1990; Novikov et al., 1990). Phosphogypsum has also been used in agriculture as a feed additive for livestock (Golushko, 1984) and as a fertilizer amendment to reduce ammonia volatilization from urea fertilizer (Boyrakli, 1990), however, use as a soil amendment has been reported most extensively.

5.1. Source of plant nutrients

In plant nutrition studies, phosphogypsum has been used as a source of Ca, S, and P on a broad range of soils differing in pH and fertility. The effectiveness of phosphogypsum as a nutrient source has been attributed to its relatively rapid dissolution rate and its capacity to supply relatively large amounts of soluble nutrients during critical phases of crop growth (Malavolta et al., 1987; Bianco et

al., 1990; Gascho and Alva, 1990; Singh et al., 1990). While P_2O_5 comprises a rather small percentage of phosphogypsum material (<1%), high application rates may significantly increase available soil P (Broadbent et al., 1989; Khalil et al., 1990).

Some studies have described the influence of phosphogypsum on the availability and uptake of other nutrients. Phosphogypsum increased the availability of Fe and Mn through a localized acidifying action around roots, and increased the availability of N, P, K, and Mg in calcareous soils (Khalil et al., 1990; Singh et al., 1990). Magnesium and/or K displaced from the exchange complex by Ca derived from phosphogypsum may be subsequently leached from the zone of interest (Pavan et al., 1987; Sumner et al., 1988; Gascho and Alva, 1990). However, excess Mg and K have been linked to peanut pod rot and leaching of these cations from the pegging zone (0–8 cm) had a beneficial effect on production (Gascho and Alva, 1990).

The beneficial effect of phosphogypsum for controlling diseases is noted in some studies. Phosphogypsum either directly influenced the reduction of phytophthora infection of citrus roots or affected plant nutrition in a way which depressed fungus development on the roots (Smith et al., 1989; Nemec et al., 1990).

5.2. Reclamation of acid soils

The need to develop practical methods to ameliorate subsoil acidity is important because many acid soils in tropical and subtropical areas are used for food production. Phytotoxic Al levels, sometimes accompanied by deficient Ca levels and/or clay hardpans, may restrict root exploitation of subsoil horizons (Shainberg et al., 1989). Crops, grown on such soils, are unable to use moisture and nutrients below ameliorated surface horizons.

When phosphogypsum is applied to acid soils, field and lab studies have found: (i) decreased levels of exchangeable and solution Al; (ii) increased levels of exchangeable and solution Ca; (iii) small and/or somewhat variable effects on pH; and (iv) enhanced root growth (Pavan et al., 1987; O'Brien

et al., 1988; Alva et al., 1988, 1990, 1991; Alva and Sumner, 1990; Mathews and Joost, 1990). The formation of less phytotoxic ion pairs and complex ions, mineral precipitation and, in some highly, weathered soils ionic strength induced adsorption were proposed as possible mechanisms for the reduction of exchangeable and solution Al (Pavan et al., 1987; Sumner et al., 1988).

Calcium exchange for H^+ and Al species, and SO_4^{2-} replacement of OH^- by ligand exchange, affect pH. In highly weathered soils, these opposing processes are often nearly balanced owing to relatively large quantities of hydroxylated surfaces on sesquioxides available for ligand exchange, as well as a low cation exchange capacity and therefore low exchangeable acidity (Shainberg et al., 1989).

Phytotoxic Al levels inhibit root growth by disrupting root cell division during mitosis. Root proliferation, as determined by root sampling and water extraction patterns, corresponded with soil zones where Al levels were reduced (Pavan et al., 1987; Sumner et al., 1988). Crop increases in phosphogypsum amended soils were apparently related to reduced phytotoxic Al levels and associated root proliferation rather than phosphogypsum induced changes in pH.

The dissolution rate of phosphogypsum partially controls its effectiveness as an amendment on acid soils and other problem soils. Factors which influence the dissolution rate include particle size, formation of a P and Al enriched skin on phosphogypsum granules, and the method of application. Coarse particles and skins can reduce the dissolution rate and the ameliorative effect of phosphogypsum (Frenkel et al., 1989b). Surface application of phosphogypsum was found to have a less beneficial effect on alfalfa yields and Al-Ca exchange reactions than deep incorporated lime (Sumner et al., 1986).

5.3. Reclamation of sodic soils

Sodic soils often exhibit poor soil structure due to the dispersion of clay particles that occur when high levels of sodium are present on the exchange complex of soils. The large, highly hydrated Na cation is less effective than smaller, divalent Ca ca-

tions at satisfying negative charges on clay surfaces; therefore, the replacement of Na with Ca reduces dispersion and promotes flocculation of soil particles. Phosphogypsum is an effective ameliorant for sodic soils because it supplies sufficient Ca to displace Na from the exchange complex of soils. Also, it has a relatively rapid dissolution rate and a relatively high solubility (Merrill et al., 1980; Okorkov, 1988; McKenzie and So, 1989a; Orlov et al., 1989).

Rates of phosphogypsum applied to sodic soils have been based on replacing a portion of the initial content of Na with an equivalent quantity of Ca. A coefficient of gypsum utilization for the displacement of Na has also been included in rate calculations (Okorkov, 1988). The gypsum utilization coefficient considers the factors which affect the efficiency and rate of Ca displacement of exchangeable Na. The percentage of Ca that exchanges for adsorbed Na will be much greater at high exchangeable Na levels (Shainberg et al., 1989).

Phosphogypsum applied at rates between 2.5 and 30 t ha⁻¹ induced replacement of exchangeable Na with Ca (Merrill et al., 1980; Petrov and Savchenko, 1986; Okorkov, 1988; McKenzie and So, 1989a) and resulted in significant reductions in the pH of alkaline, saline, and saline-sodic soils (Mishra, 1980; Orlov et al., 1989). The flocculating effect of Ca on soil particles was found to decrease bulk density, increase porosity, and promote formation of soil structure and aggregate stability (Orlov et al., 1989). These changes in soil physical properties generally enhanced water infiltration and leaching of Na. The amount of infiltrating water, texture and initial hydraulic conductivity of soils were factors reported to affect the extent of leaching.

5.4. Erosion control

Erosion control studies have investigated the interrelated effects of phosphogypsum, precipitation and slope characteristics on soils which exhibit a tendency to disperse and form crusts. These soils are characterized by having high sodicity at the surface, or by containing highly weathered, non-sodic kaolinitic and illitic clays which disperse

when water with a low electrolyte concentration is applied (Agassi et al., 1985, 1986, 1990; Miller, 1987; Stern et al., 1991). In general, crusting reduces infiltration and increases runoff and soil loss.

The dispersion process is due, in part, to a chemical mechanism which depends on the exchangeable sodium percentage and the electrolyte concentration of the applied water. The dispersed clay particles may be deposited in the upper few millimeters of the soil (Gal et al., 1984; Frenkel et al., 1989a) or are carried off as sediment in runoff. A second complementary mechanism involves the physical disintegration of surface aggregates under raindrop impact (Stern et al., 1991). When water of high electrolyte concentration is used, chemically induced dispersion is largely prevented and a thin seal with high permeability is formed, mainly by the physical mechanism (Agassi et al., 1985; Frenkel et al., 1989a).

Phosphogypsum application to soil mainly affects the dispersion process by rapidly introducing electrolytes including Ca, into the applied water at the soil surface. This promotes flocculation, enhances aggregate stability and deposition of entrained particles in runoff (Warrington et al., 1989; Agassi et al., 1985, 1990; Agassi and Ben-Hur, 1991). However, phosphogypsum may also inhibit physical disintegration by acting as a mulch to intercept and reduce the impact of raindrops. In general, application of phosphogypsum increases infiltration, decreases runoff, and decreases soil loss compared to control treatments.

The relative effectiveness of phosphogypsum for reducing erosion is partially dependent on the impact energy of rainfall at the soil surface (Smith et al., 1990). Other factors include slope gradient and length, application rate and method, and other agronomic practices. Agassi et al. (1990) found that the beneficial effect of phosphogypsum was less pronounced when the impact of raindrops decreased. The capability of phosphogypsum to supply sufficient electrolytes to inhibit dispersion during storms depends on the amount, intensity, and duration of rainfall of preceding storms (Stern et al., 1991). Agassi et al. (1985) reported that phosphogypsum reduced runoff by 76% compared

with control treatments, even after 528 mm of rainfall. In another study, beneficial effects lasted until the cumulative rain exceeded 700 mm (Stern et al., 1991). This long lasting effect is partially due to return of some of the gypsum to the soil surface through capillary rise during drying periods.

Soil loss increases with increased slope gradient. Runoff and soil loss has been reported to be less in phosphogypsum amended versus control treatments when the slope gradient increased (Agassi et al., 1985, 1989; Warrington et al., 1989). The difference in runoff between the phosphogypsum and the control treatments decreased as the slope increased. Apparently, the greater amount of erosion on control plots removed seal material which led to enhanced infiltration and decreased runoff as the slope increased (Agassi et al., 1985; Warrington et al., 1989).

A single, broadcast application of phosphogypsum at 5 t ha⁻¹ was considered to be the most effective amendment in terms of water use efficiency; although a phosphogypsum broadcast at a rate of 10 t ha⁻¹ resulted in the greatest cumulative infiltration and final infiltration rate. The effectiveness of phosphogypsum in preventing crust formation is reduced when it is incorporated; however, broadcasting phosphogypsum as a fine powder may expose it to wind erosion (Agassi et al., 1985).

Phosphogypsum has been compared to other amendments and agronomic practices designed to improve soil physical properties. Mulching with corn stover (3 t ha⁻¹) (Stern et al., 1991), straw (80% cover) (Frenkel et al., 1989a), and spray applications of polyacrylamide solution helped prevent physical disintegration of aggregates and were found to be more effective for controlling runoff than was phosphogypsum. The combined application of phosphogypsum and polyacrylamide had a synergistic effect on reducing runoff (Smith et al., 1990; Stern et al., 1991). Phosphogypsum was more effective in reducing runoff and erosion in potato fields than a diked furrow tillage treatment (Agassi et al., 1989). Fuel consumption, an indication of the ease of tillage, was reduced for disking and weeding operations following a 7.5 t ha⁻¹ application of phosphogypsum (McKenzie and So, 1989b).

6. Environmental concerns related to the agricultural use of phosphogypsum

6.1. Radionuclide uptake by plants and radioactive buildup in soil

Radionuclides have been reported to be taken up by agricultural plants from soil contaminated by uranium processing wastes (Tracy et al., 1983) and mined phosphate lands (Guidry et al., 1986, 1990); hence, there is some concern that the application of phosphogypsum to agricultural lands may result in the uptake of radionuclides by food crops. Radionuclide uptake is influenced by soil factors and the type of plant species. Root crops, leafy vegetables and legumes tend to take up more radionuclides than fruit bearing plants (Tracy et al., 1983; Guidry, 1986).

Only a few studies have reported the radionuclide uptake by plants grown on phosphogypsum amended soils. May and Mordvedt (1986) applied up to 112 mg ha⁻¹ of phosphogypsum containing 925 Bq kg⁻¹ of Ra-226 to soil which was used to grow corn, wheat, and soybeans in rotation. No increases in grain Ra-226 were detected in any of the crops, although levels in the surface soil were increased from 35 Bq kg⁻¹ to 73 Bq kg⁻¹. Arkhipov et al. (1984) found that rates up to 20 t ha⁻¹ increased soil levels of radionuclides, but uptake and accumulation of radionuclides in wheat grain was only slightly higher than in control treatments. In another study, radioactivity determinations of sugarcane juice showed no significant difference in counts among background, control, and phosphogypsum treated areas (Golden, 1983). Relatively low application rates (<293 kg ha⁻¹) had little, if any, effect on Ra-226 and Po-210 levels in forage and soil samples (Mullins and Mitchell, 1990). Radium-226 and Pb-210 have been found to be significantly increased in plants grown on reclaimed phosphate mine lands (Guidry et al., 1990). However, the total radionuclide content in the root zone of these soils was at least an order of magnitude greater than what would be contained in a very heavy phosphogypsum application (i.e., 100 t ha⁻¹). It was estimated in the study by Guidry et al. (1990) that a person who obtained all of his or her leafy

vegetables, root vegetables, peas and beans from the phosphate mined lands would receive an effective dose equivalent of 19.1 mrem/year which is not considered to be a health hazard.

A few authors have conducted theoretical radiological assessments of radionuclide buildup in soil and uptake by plants from phosphogypsum applications. Lindeken (1980) described a scenario where phosphogypsum of 0.56 Bq g^{-1} Ra-226 content was applied to soil at an initial rate of 10 tons acre^{-1} followed by alternate year applications of 5 tons acre^{-1} . If all the Ra-226 remained in the surface 6 inches, the proposed federal concentration limit of 0.19 Bq g^{-1} soil (federal concentration limit to lands contaminated by uranium tailings on which residences may be constructed) would not be reached for 100 years. Assuming a concentration ratio (radium in dry foodstuff to radium in soil) of 0.01 for crops growing on land containing $0.19 \text{ Bq Ra-226 g}^{-1}$ soil, and assuming human consumption of 80 g day^{-1} , the integrated 50-year radiation dose to the bone would be 1.4 rem. The allowable annual dose for unrestricted persons is approximately 2 rem (Lindeken, 1980). It should be noted that the National Council of Radiation Protection (NCRP, 1984) guideline for restricting soil for the use of growing human food crops is a Ra-226 content of 1.5 Bq g^{-1} soil.

Roessler (1988) conducted a detailed radiological assessment to evaluate the extent to which the radioactivity originating from phosphogypsum applied to soil would appear in crops and contribute to human radiation exposure. In one scenario, phosphogypsum containing 1.1 Bq g^{-1} Ra-226 was applied at a rate of 1 ton acre^{-1} once every 4 years and tilled to a depth of 15 cm. Assuming a 2% loss of Ra-226 from the root zone per year by erosion or leaching the equilibrium application concentration would be 0.014 Bq g^{-1} , which would be 90% of that attained after 100 years. Roessler (1988) assumed a very conservative concentration ratio of 1 but placed an upper concentration of $9 \text{ Bq Ra-226 kg}^{-1}$ grain dry matter based on earlier observations with other Ra-226 bearing materials. Typical values for U.S. grain products are $0.081\text{--}0.093 \text{ Bq kg}^{-1}$ (McDowell-Boyer et al., 1979). A person whose sole source of consumed grain products originating from food

grown on phosphogypsum-treated land would consume approximately 1.9 Bq day^{-1} of Ra-226 and would receive a bone surface dose of $300 \text{ mrem year}^{-1}$ and a committed effective dose equivalent (CEDE) of $20 \text{ mrem year}^{-1}$. This intake level is about 50 times greater than the typical dietary uptake and 2.5 times greater than the Federal Radiation Council guidance. The $20 \text{ mrem year}^{-1}$ CEDE is 20% of the NCRP recommendation for continuous exposure to an individual of the general public. Roessler (1988) went on to say that these projected intakes and doses are significant but are probably overestimated because it is unlikely that total grain product intake would originate from phosphogypsum treated land. Also, high values were chosen with respect to Ra-226 concentration in plants, intake and dose. It was concluded that the proposed application of phosphogypsum to soil used for grain production would not pose a problem for tens of years although it would be difficult to extrapolate beyond 50 years because some factors were not well defined.

One important factor in the use of phosphogypsum on agricultural lands is the possibility of raising the overall radioactivity of the soil such that it becomes unsuitable for other uses. Thus, even though crops may be consumed from lands treated with phosphogypsum, the land may become unsuitable for residential use due to the potential radon risk in basements. Lindeken (1980) determined that a Ra-226 concentration of 0.19 Bq g^{-1} soil would generate radon daughter concentrations which exceed proposed guidelines for residential occupancy. May and Mordvedt (1986) raised soil Ra-226 from 0.035 to 0.073 Bq g^{-1} after one heavy application of phosphogypsum, thus a few more applications at these high rates would likely result in the guideline levels being exceeded. Recently the U.S. E.P.A. ruled that phosphogypsum would only be permitted for use in agriculture if the average concentration of Ra-226 in the phosphogypsum does not exceed 370 Bq kg^{-1} (Federal Register, 1992). This limit was set to assure that the risks due to indoor radon and direct gamma radiation in residences constructed on land previously treated with phosphogypsum do not exceed an acceptable level.

6.2. Non-radioactive element uptake by plants

The potential uptake of fluoride and trace elements derived from phosphogypsum are potential environmental concerns. Phosphogypsum applications of 10 or 20 t ha⁻¹ did not result in accumulation of high fluoride concentrations in soil and plants (Petrov and Savchenko, 1986). Even if phosphogypsum application rates are large enough to cause high fluoride concentrations in the soil, some acid soil studies have shown or suggested that most of the fluoride would be adsorbed in the topsoil (Shainberg et al., 1989; Alva et al., 1990). Few studies have examined heavy metal uptake by plants from phosphogypsum treated soil. May and Mortvedt (1986) reported that very high rates of phosphogypsum application did not have any effect on Cd uptake in a corn-wheat-soybean cropping sequence, however, the Cd concentration of the phosphogypsum was only 0.23 µg g⁻¹. Typical soil levels are 0.35 µg g⁻¹ (Sposito, 1989).

6.3. Other concerns

Phosphorus contamination of surface waters as a result of land application of phosphogypsum is also a concern regarding the agricultural use of phosphogypsum. The results of a laboratory rainfall simulator study suggested that application of high phosphogypsum rates may result in P being exported into waterways adjacent to the sites of application and hence it may contribute to the enhanced eutrophication of the waterways (Korentajer et al., 1991).

7. Conclusions

Very large quantities of phosphogypsum have been produced world-wide since the 1950s because of the high demand for phosphate fertilizer, and because the wet phosphoric acid process produces about 5 tonnes of phosphogypsum for every tonne of phosphoric acid manufactured. Most of the phosphogypsum produced world-wide is stockpiled. Much interest has focused on finding uses for this by-product, such as a soil amendment for the remediation of problem soils. There are still unanswered questions about the environmental implications associated with the storage and agricultural use of phosphogypsum.

The main environmental concerns related to the storage and agricultural use of phosphogypsum are summarized in Fig. 3. Research has determined that acidity, F⁻, SO₄²⁻, certain trace elements and certain radionuclides may be elevated in the waste product and have the potential to be mobile in the environment. Both the acidic process water and the phosphogypsum itself are potential sources of contamination. Much concern is related to the possible contamination of groundwater under phosphogypsum stacks, and to radon exhalation which may pose a health risk to people working on or living close to a stack. Atmospheric F⁻ can be a significant contaminant from phosphate fertilizer manufacturing; however, most process plants use scrubbers to reduce gaseous F⁻ levels to within acceptable levels. Some authors predict that employees working on phosphogypsum stacks are at low risk from direct gamma radiation originating from the stacks, or from inhalation of phosphogypsum dust under normal weather conditions. The largest concern related to the use of phosphogypsum as an amendment to agricultural soils is not plant uptake of radionuclides but the risk of elevated indoor radon levels if the agricultural land is later converted to residential usage. For this reason the U.S. E.P.A. has ruled that no phosphogypsum may be used as a soil amendment if its Ra-226 content exceeds 370 Bq kg⁻¹.

The leachate chemistry of the radionuclides is of major importance in determining the environmental impact of phosphogypsum. It is generally believed that most Ra-226 in phosphogypsum exists as a sulfate compound in solid solution with Sr and Ba, however, the physical location of Ra-226 is not clearly resolved. Moisset (1988) found distinct crystals very rich in co-crystallized Ra-226, but some Ra-226 might also be present within the small quantities of hemihydrate that are contained in dihydrate phosphogypsum. Further clarification of the chemical form and physical location of Ra-226 in phosphogypsum may help explain its chemical behavior (Rutherford et al., 1994).

Although Ra-226 is considered to be the main source of radioactivity in phosphogypsum, other U-238 series radionuclides may be present in signi-

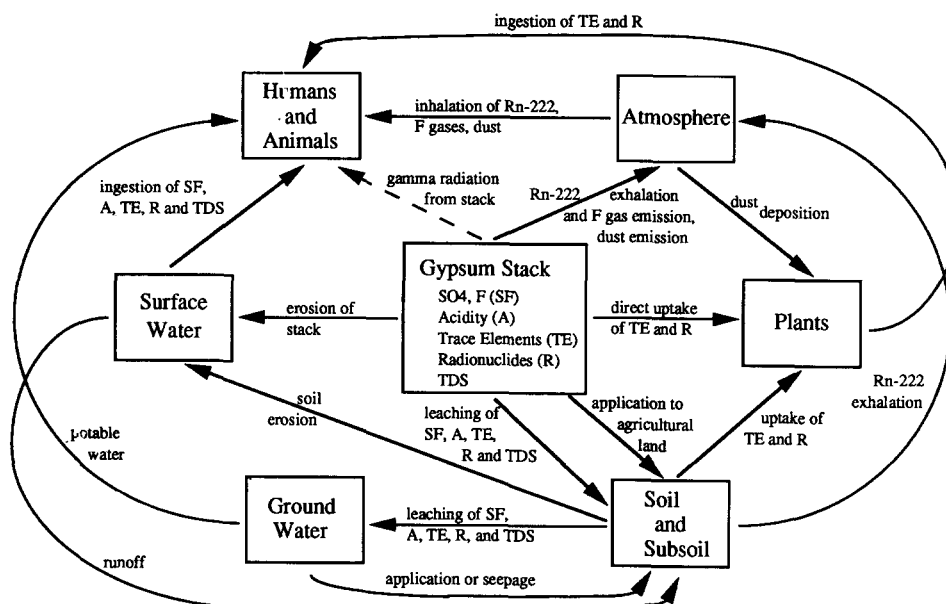


Fig. 3. Main environmental concerns due to the storage and agricultural use of phosphogypsum.

ficant quantities (Table 5). Alpha emitting radionuclides are more of a concern than beta emitters because they do more biological damage once they are inhaled or ingested. Uranium content in phosphogypsum can be quite variable, depending on phosphoric acid plant conditions. Some references have reported U-238 activities equal to that of Ra-226. This is a concern because U(VI) can be highly mobile in the environment. Polonium-210 is a relatively long-lived radionuclide (138 days) which is partitioned into phosphogypsum during the wet phosphoric acid process. Few studies have reported Po-210 chemistry in phosphogypsum, even though it has been found to be the major alpha emitting radionuclide in groundwater under phosphate mined lands. The chemistry of Po-210 is not clearly understood (Upchurch et al., 1991) and therefore requires further investigation. Practices which increase the carbon content and/or biological activity in phosphogypsum, such as the establishment of soil and vegetation caps on stacks, may increase radionuclide mobility due to the production of microbial chelating agents

(Birch and Bachofen, 1990). Further research is required to elucidate radionuclide behavior in phosphogypsum and in phosphogypsum-treated soil.

The exhalation of Rn-222 from phosphogypsum stacks may vary by several orders of magnitude, ranging from <0.004 to $>3 \text{ Bq m}^{-2} \text{ s}^{-1}$. Because the U.S. E.P.A. recently adopted an average $0.74 \text{ Bq m}^{-2} \text{ s}^{-1}$ upper limit on Rn-222 emissions from phosphogypsum stacks it is important for companies to monitor their stacks and be aware of the variables which affect Rn-222 exhalation. Most studies have concluded that populations living close to phosphogypsum stacks are not subjected to a significant health risk because air movement readily dilutes Rn-222 concentrations. It is still not clear whether employees who spend numerous hours on active phosphogypsum stacks are subjected to a significant health risk. There is not much published literature on the effects of soil caps and vegetation cover on the release of Rn-222 from phosphogypsum surfaces.

There have been some inconsistent reports

regarding the mobility of phosphogypsum constituents. Some laboratory studies have concluded that significant levels of contaminants do not leach from phosphogypsum, however some field studies have found elevated levels of F^- , SO_4^{2-} , acidity, trace elements, radionuclides and total dissolved solids in groundwater near phosphogypsum stacks. Clearly, further research is required to improve our understanding of the geochemistry occurring within, and beneath, phosphogypsum stacks. To accomplish this it is necessary to identify the solubility-controlling solids of the elements contained within phosphogypsum, especially those for trace elements and radionuclides (Eary et al., 1990). It is also necessary to determine which conditions (e.g. redox, pH and ionic strength) exist within, and beneath, phosphogypsum stacks in order to predict the dominant chemical species present. It is also important to identify the reactions which occur when contaminants originating from phosphogypsum contact soil materials to determine if attenuation occurs before chemical species contact groundwater.

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