Wastes of Phosphate and Potash Ores

7.1 Introduction

Plants and agricultural crops require phosphorus, potassium, and nitrogen as macronutrients. In order to maintain agricultural crop yields, these elements must be added to replace those lost from the soil. In most cases, the nutrients are added to agricultural land as mineral fertilizers (UNEP/IFA 2001). Nitrogen fertilizers are generally produced from atmospheric nitrogen, water, and energy. In contrast, the production of phosphate and potassium fertilizers relies on the provision of phosphate rock and potash ores. The majority of mined phosphate rock and potash ore is processed to fertilizer; a minor proportion of the mined material is used for other purposes. World population growth and the necessity to provide adequate food supplies have resulted in the significant growth of phosphate and potash mining, and fertilizer consumption over the last 100 years. This growth has also led to the ever increasing volume of phosphate and potash mine wastes.

In this chapter, potash and phosphate deposits will be introduced prior to the documentation of the different wastes accumulating at potash and phosphate mines. This is because an understanding of phosphate and potash mine wastes requires a knowledge of their ore deposits since ore properties influence the characteristics of mine wastes. As many of the waste disposal problems and environmental impacts of phosphate mining and fertilizer manufacturing are centered on phosphogypsum, particular emphasis is placed on this topic.

7.2 Potash Mine Wastes

Potash is a generic term which refers to a number of potassium salts including carbonate, sulfate and chloride compounds. The production of potash and other salts principally relies on the mining of evaporitic salt deposits. As with all mining, mineral processing and metallurgical activities, the exploitation of salt ores not only generates mineral resources but also mine wastes. Salt ores have the specific issue of salinity and hence, potash mine wastes are invariably saline. This property differentiates potash mine wastes from other mine wastes. Appropriate disposal and rehabilitation strategies of potash mine wastes should ensure that these wastes do not release salinity into the environment and cause significant environmental harm.

7.2.1 Potash Ores

Potash is mined from potash deposits and as a by-product from rock salt (i.e. halite) ores. The nature of these deposits largely stipulates the mining method. Potash and rock salt mines are underground operations and less commonly, in situ solution mining operations. Gypsum, anhydrite, and halite are the main minerals in potash and rock salt ores. In rock salt deposits, halite is extracted as a primary product whereas potassium (sylvite: KCl; carnallite: KMgCl₃ \cdot 6 H₂O; polyhalite: K₂Ca₂Mg(SO₄)₄ \cdot 2 H₂O) and magnesium salts (kieserite: MgSO₄; tachyhydrite: CaMgCl₄ \cdot 12 H₂O) are of lesser abundance. Nonetheless, the concentrations of these less common potassium minerals in rock salt deposits provide important potash resources. In potash deposits, the ores contain sylvite and/or carnallite as dominant potassium minerals, and halite is a by-product. Gangue minerals in these deposits include clay minerals, sulfides, carbonates, iron oxides, and numerous evaporative salts. The potassium ore minerals contain variable K₂O concentrations (sylvite 63.2 wt.% K₂O; carnallite 16.9 wt.% K₂O). Potassium ore grades are expressed in terms of potassium oxide (K₂O), and currently mined potassium ores have 8 to 30 wt.% K₂O (Rauche et al. 2001).

7.2.2 Mining and Processing Wastes

Mineral processing of potash and rock salt ores involves flotation of the crushed salt ore. The flotation technique aims to concentrate the salt minerals and to reject the gangue phases. Alternatively, dissolution of the entire crude salt occurs by hot aqueous solutions, and the salts are precipitated (Rauche et al. 2001). Consequently, potash and rock salt mining produces very little mining waste whereas mineral processing results in the rejection of the majority of the mined ore as liquid and solid wastes (Ripley et al. 1996; UNEP/IFA 2001). In particular, potash ores generate more waste than any other salt ores. The major waste products of potash and rock salt processing include:

- Brines. The liquid waste from potash and rock salt operations is a saline solution. This brine can be enriched in one or more of the ore elements/compounds including calcium, potassium, sodium, magnesium, chloride, and sulfate. Disposal techniques for brines vary (Fig. 7.1). The solution may be disposed of by: (a) reinjection into deep aquifers below the orebodies; (b) discharge into the ocean; (c) collection in large ponds, treatment, and release into local rivers; or (d) pumping with or without the solid residues back into the underground workings and emplacement as hydraulic backfill (Ripley et al. 1996; Rauche et al. 2001; UNEP/IFA 2001). At shallow underground salt mines, the backfill disposal practice prevents surface subsidence which could otherwise occur in these highly ductile and leachable ore environments.
- Tailings. Solid processing wastes of potash and rock salt deposits contain rejected gangue minerals and mineral processing salts. These tailings may be backfilled into underground workings or are stacked near the mine site into large piles (Fig. 7.2) (UNEP/IFA 2001). The relative ease with which salt minerals dissolve requires that



Fig. 7.1. Potash mining operations at Unterbreizbach, Germany. Dry salt tailings have been stacked into piles, and retention ponds allow the controlled release of brines into the local river



Fig. 7.2. Potash tailings stack at Röhrigshof, Germany

piled tailings are covered with appropriate impermeable barriers (e.g. topsoils, clay seals). Alternatively, the tailings may be topped with a leached layer that acts as a suitable substrate for vegetation (Ripley et al. 1996).

7.3 Phosphate Mine Wastes

7.3.1 Phosphate Rock

Phosphate rock is defined herein as a rock containing phosphate minerals in high enough concentrations to be mined commercially. Phosphate resources exploited commonly exceed 20 wt.% P_2O_5 . Phosphate rock occurs in various deposit types, and the

principal industrial mineral of all deposits is apatite in the form of fluorapatite $(Ca_5(PO_4)_3(F))$ and/or carbonate fluorapatite $(Ca_5(PO_4)_3CO_3)_3(F))$. Exploitable phosphate deposits can be divided into three types: phosphorites; carbonatites and alkaline igneous rocks; guano deposits. Of these deposits, phosphorites constitute the predominantly mined ore.

- 1. *Phosphorites*. Phosphorites or marine sedimentary phosphate deposits contain carbonate fluorapatite with 1 wt.% fluorine and appreciable amounts of carbonate as the phosphate mineral (e.g. USA, Morocco, Togo, Egypt, eastern Australia). This apatite form is also referred to as francolite. The francolite is present as nodules or pellets up to several millimeters in diameter which may contain various impurities. The impurities occur as physical inclusions (e.g. quartz, clays, iron oxyhydroxides, organic matter, carbonates) or as crystallographic substitutions within the phosphate mineral. Ions which will substitute for calcium, phosphate and fluorine within the francolite lattice are diverse and mainly include sodium, magnesium, strontium, carbonate, and sulfate as well as various trace elements (e.g. U, Th, REE, Y, Cd, Zn) (Jarvis et al. 1994; Rutherford et al. 1994). Trace heavy metal and metalloid enrichments (e.g. Ag, As, Cd, Cu, Mo, Ni, Sb, Se, V, Zn) of phosphorites are associated with abundant organic matter. The enrichment is likely due to the adsorption or incorporation of these elements in organic substances or sulfides.
- 2. Carbonatites and alkaline igneous rocks. Carbonatites and other alkaline igneous rocks commonly contain elevated phosphate concentrations in the form of fluorapatite (e.g. Russia, Canada). Weathering of these igneous rocks removes soluble carbonate minerals and leads to the natural concentration of fluorapatite and other weathering resistant minerals (e.g. magnetite, pyrochlore). Deep weathering profiles overlying and derived from carbonatites are known to contain distinctly elevated phosphate concentrations in the form of fluorapatite (e.g. western Australia, Brazil). Secondary aluminophosphate minerals such as crandallite (CaAl₃(PO₄)₂(OH)₅H₂O) may form during weathering of the apatite. These crandallite-rich horizons are not suitable for phosphate extraction.
- 3. *Guano deposits*. Guano deposits on tropical coral islands represent originally bird excrements which have been leached, oxidized, and redeposited as amorphous and crystalline phosphates. Commercial guano deposits have largely been mined out, and there has been no production of mining or processing wastes on site due to the nature of the deposits. Some of the mined deposits require extensive rehabilitation (e.g. Christmas Island, Nauru, Ocean Island). For example, phosphate mining on the island of Nauru has disturbed land to such an extent that only the coastal fringe of the island remains habitable.

The presence of elevated radionuclide, arsenic, cadmium, selenium and thallium concentrations in some guano and phosphorite deposits can limit the use of these deposits. Fertilizers manufactured from such deposits will contain elevated concentrations of these elements (Lottermoser and Schomberg 1993; Jarvis et al. 1994). Cadmium, in particular, can accumulate in soils and plants through repeated fertilizer use, and fertilizer application to agricultural land may result in the transfer of cadmium into the food chain. Cadmium-rich phosphorites are considered to be unsuitable for fertilizer production, and the application of cadmium enriched fertilizers has been restricted

in some countries. Also, fertilizers contain trace quantities of uranium, and the application of fertilizer to agricultural land and soil erosion add uranium to local waterways and oceans. For instance, the Everglade wetlands and the Mediterranean Sea contain fertilizerderived uranium due to phosphate fertilizer inputs (Ragnarsdottir and Charlet 2000).

7.3.1.1 Mineralogy and Geochemistry

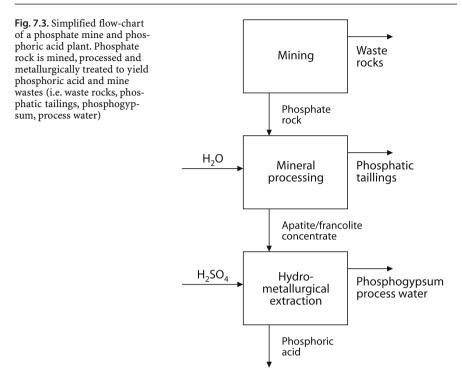
The principal mineral of all ores is apatite while the gangue mineralogy of phosphate deposits is deposit specific. Gangue minerals include framework, ortho, ring, chain and sheet silicates as well as sulfides, oxides, hydroxides, sulfates, and carbonates. The variation in gangue mineralogy causes the major and trace element geochemistry of phosphate deposits to be variable. In particular, phosphorite deposits tend to possess elevated uranium, thorium, rare earth element, yttrium, heavy metal and metalloid values (Jarvis et al. 1994). Carbonatite and alkaline igneous rock related deposits display high uranium, thorium, rare earth element, yttrium, niobium, tantalum, titanium and zirconium concentrations.

Some phosphate deposits have elevated radioactivity and radon levels (Rutherford et al. 1994). The radioactivity and radon originate from abundant uranium and thorium, and the daughter nuclides of the U-238, U-235 and Th-232 decay series (Table 6.2). Uranium and thorium concentrations of phosphate deposits are highly variable, and igneous deposits tend to contain lower uranium and higher thorium levels than sedimentary phosphorites. Beneficiation of phosphate rocks not only leads to concentration of the phosphate minerals but also to the concentration of the specific radioactivity (Ci kg⁻¹) contained in the phosphate rock. Most of the radioactive nuclides are likely hosted by the apatite crystal lattice or are adsorbed onto surfaces of clays and organics (Burnett et al. 1995). On the other hand, some radionuclides, such as Ra-226, have ionic radii and charges which are not commensurate with the size and charge of the host calcium cation of apatite. As a consequence, Ra-226 may be present in separate barium-strontium sulfate phases (Rutherford et al. 1994).

7.3.2

Mining, Processing and Hydrometallurgical Wastes

Due to the nature of many phosphate deposits, *waste rocks* or *overburden* must be removed to extract the ore. The mined rock is then processed with water to remove unwanted gangue minerals and to concentrate the phosphate minerals to a raw material for phosphoric acid production. The processing generates a phosphate mineral concentrate and unwanted fine-grained rock and mineral particles. These *tailings* are either discarded in tailings ponds or are discharged into rivers and oceans. The production of phosphoric acid is commonly achieved by dissolving the washed and concentrated phosphate minerals in sulfuric acid. The unwanted by-product of such fertilizer manufacturing is referred to as "*phosphogypsum*". In many cases, fertilizer plants have been built adjacent to, or in the vicinity of, phosphate mines. As a result, vast quantities of phosphogypsum accumulate at phosphate mine sites. Wastes of phosphate mining, processing and metallurgical extraction can be grouped into the following four main categories (UNEP/IFA 2001) (Fig. 7.3):



- 1. Waste rocks. Mining of phosphate deposits produces phosphate rock which is either used as rock phosphate fertilizer or is further processed to phosphoric acid for fertilizer manufacturing. The mining activities invariably generate waste rocks. These are country rocks enclosing phosphate deposits, and they need to be mined to access the deposit. The wastes possess no or subeconomic amounts of apatite and display low phosphate concentrations and thus, low radioactivity and radon levels. Sulfide contents are highly variable and deposit specific. Highly sulfidic waste rocks may generate AMD, and such waste materials require appropriate characterization, prediction, monitoring, and control (Chap. 2). Mined waste rocks are commonly disposed of in piles near the mine. The long-term stability of waste rock dumps is of prime concern, especially for those piles constructed in areas with high erosion rates. Such dumps require monitoring for erosional stability; the non-sulfidic wastes do not need other monitoring strategies, treatment of seepages or installation of covers. If wastes contain significant quantities of metals and metalloids (e.g. Ag, As, Cd, Cu, Mo, Ni, Sb, Se, V, Zn), leachates with significant metal and metalloid concentrations may be formed (Vance 2000). In most cases, however, the waste rocks are benign wastes and do not pose an environmental threat. They contain naturally elevated nutrient concentrations, so the revegetation of non-sulfidic waste rock dumps is easily achieved. Phosphatic waste rocks may even be put to good use and be consumed in the rehabilitation of mine sites and waste repositories (e.g. landscaping, capping, revegetation).
- 2. *Phosphatic tailings*. The mined phosphate rock is commonly treated prior to phosphoric acid manufacturing. Mineral processing of phosphorites usually involves a

combination of various treatment techniques. The beneficiation aims: (a) to remove fine-grained rock and mineral particles as slimes; (b) to remove coarse-grained quartz sand particles as sands; and (c) to concentrate the apatite. Organic-rich phosphate rock may have to be heated prior to processing in order to reduce the organic matter content to acceptable levels. The rejected gangue minerals include calcite, dolomite, quartz, clays, iron oxides, and aluminium and iron phosphates. The wastes are in the sand to clay size range and are termed "phosphatic tailings". Thus, phosphatic clays and sands accumulate during the beneficiation of phosphorites. The sand particles may be pumped to storage impoundments, or they may be reclaimed and used as a backfill of mine workings. The clay particles - liberated during benefication - are either disposed of to rivers, mined-out areas or engineered storage impoundments. Beneficiation of particularly clay-rich phosphorites results in the production of exceptionally fine-grained particles and colloids. Such phosphatic clays are also referred to as "fines" or "slimes". The production of slimes is, of course, minimal for those deposits where the clay content is volumetrically insignificant. Phosphatic clays have poor settling characteristics and require long periods to settle without any treatment. Settling of these slimes may require construction of large ponds covering vast areas, and even larger settling ponds are needed for those deposits containing large quantities of clays (e.g. Florida). The settling time of the slime particles and colloids can be accelerated to some degree using flocculants, which are added to the slurry upon discharge to the ponds. Sludge ponds may, therefore, contain chemicals used as reagents in the flotation process. These chemicals include soda ash, diesel, fatty acid, ammonium hydroxide, sodium silicate, sulfuric acid, and amine.

- 3. *Phosphogypsum.* The greatest volume of waste products is generated in the phosphoric acid plant where the extraction of phosphorus from beneficiated phosphate rock is conducted (Fig. 7.4). The production of phosphoric acid is achieved by thermal reduction of the phosphate rock in an electric furnace to produce elemental phosphorus (i.e. pyrometallurgy), or more commonly by the chemical reaction of the phosphate rock with sulfuric acid (i.e. hydrometallurgy). The latter, so-called "wet process", not only results in the production of phosphoric acid but also in the generation of *process waters* and *phosphogypsum* waste. The most common manufacturing process for phosphoric acid is based on the use of sulfuric acid, which results in the production of phosphoric acid manufacture, about 3 to 6 t of phosphogypsum are generated for every tonne of phosphoric acid produced. The phosphogypsum is a substantial waste product of the fertilizer producing industry and is commonly stored in very large piles near the processing plants.
- 4. *Process water.* Spent process waters are disposed of with the phosphogypsum and are commonly pumped to the phosphogypsum repository. Hence, phosphogypsum dumps contain very low pH (as low pH 1), high TDS process waters with potentially elevated fluoride, sulfate, phosphate, ammonia, radionuclide, heavy metal and metalloid concentrations. Such waters require isolation within the waste repository or collection in lined ponds. Excess process waters may need to be neutralized with lime prior to their discharge to receiving streams. Sludges generated from the neutralization process generally require isolation, for example, in the phosphogypsum stack (Ericson et al. 1997).

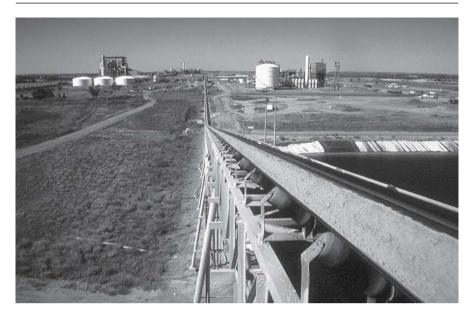


Fig. 7.4. View of parts of the fertilizer production facility at Phosphate Hill, Australia. Ammonia plant (*far right*), phosphoric acid facility (*centre*), granulation plant (*left*), and rail loadout facility (*far left*). A conveyer belt delivers phosphogypsum to the stack

7.3.3 Phosphogypsum

In the wet process, the ground phosphate rock concentrate $(Ca_5(PO_4)_3(F))$ is reacted with sulfuric acid (H_2SO_4) to produce phosphoric acid (H_3PO_4) and calcium sulfate crystals $(CaSO_4 \cdot 2H_2O)$. These calcium sulfate solids are referred to as phosphogypsum. Other reaction products include hydrofluoric acid (HF). The reaction of phosphate rock with sulfuric acid can be written as follows:

$$Ca_{5}(PO_{4})_{3}(F)_{(s)} + 5 H_{2}SO_{4(aq)} + 10 H_{2}O_{(l)} \rightarrow 3 H_{3}PO_{4(aq)} + 5 CaSO_{4} \cdot 2 H_{2}O_{(s)} + HF_{(aq)} + heat$$
(7.1)

7.3.3.1 Mineralogy and Geochemistry

The above chemical reaction (Reaction 7.1) illustrates the manufacturing process of phosphoric acid and the production of calcium sulfate (i.e. phosphogypsum), yet it does not adequately account for other reaction products. The calcium sulfate can be produced in different mineralogical forms. Depending on the manufacturing process, the phosphoric acid production can result in the formation of phosphogypsum in the dihydrate (gypsum: $CaSO_4 \cdot 2H_2O$) or hemihydrate (bassanite: $CaSO_4 \cdot 0.5H_2O$) form (Rutherford et al. 1994). The dihydrate form is the most common waste product; hemihydrate is metastable in water and may convert in time to dihydrate.

Phosphogypsum dominantly consists of calcium sulfate crystals. It also contains other small solid phases. These include reaction products of the wet process (e.g. alkali fluosilicates, fluorides) and unreacted phosphate rock and gangue mineral particles (e.g. quartz, phosphates, organic matter, feldspars) (Luther et al. 1993; Rutherford et al. 1995; Arocena et al. 1995a). In addition, the calcium sulfate crystals contain liquid inclusions and process waters trapped in the interstices of mineral particles. The pore liquids are variably enriched in phosphoric acid, sulfuric acid, fluorine, nitrate, heavy metals, metalloids, and radionuclides (Luther et al. 1993). The term "*phosphogypsum*" is, therefore, a collective term for a waste mixture comprising major solid and minor liquid waste components.

Phosphogypsum has physical and chemical properties broadly similar to natural gypsum and bassanite. Phosphogypsum readily dissolves in rainwater in a similar way to gypsum, and its dissolution is independent of pH. In contrast, the properties of an entire phosphogypsum pile are dissimilar to those of a natural gypsum mass of the same size. A phosphogypsum pile contains numerous very fine-grained phosphogypsum particles. The total specific surface area (i.e. $m^2 g^{-1}$) of all phosphogypsum particles is exceptionally large and as a result, the phosphogypsum pile dissolves more rapidly than a gypsum mass of the same size. Thus, mineralogical properties influence the performance of phosphogypsum dumps. If a closed, uncapped phosphogypsum pile is continuously exposed to rainwater infiltration, the dump will develop karst features such as solution channels and cavities.

The chemical composition of phosphogypsum can vary greatly depending on: (*a*) the nature of the phosphate rock used in phosphoric acid manufacturing; (*b*) the type of wet phosphoric acid process used; (*c*) the efficiency of the plant operation; and (*d*) any contaminants which may be introduced into the phosphogypsum during manufacturing (Rutherford et al. 1994). Major compounds of phosphogypsum are calcium and sulfate (Table 7.1). Significant trace constituents include fluorine, rare earth elements, heavy metals, metalloids, and radionuclides (Table 7.2). The material is acidic due to the presence of residual phosphoric, sulfuric and fluoride acids. Prolonged leaching of phosphogypsum in stacks leads to the flushing of trapped acids, heavy metals, and metalloids. Hence, aged and leached materials display near neutral pH and lower trace element values.

The siting of trace elements, metals and metalloids in phosphogypsum is variable. For instance, it has been suggested that: (*a*) cadmium and strontium may substitute for calcium in the calcium sulfate crystal lattice; (*b*) uranium may be adsorbed onto the surface of calcium sulfate crystals; (*c*) selenium may be adsorbed onto iron oxyhydroxides; and (*d*) silver may form discrete halide minerals (Rutherford et al. 1994; Arocena et al. 1995a). The finer particle fraction (<20 µm) of phosphogypsum tends to have higher fluorine, heavy metal, metalloid and radionuclide concentrations than coarser size fractions (Rutherford et al. 1994; Arocena et al. 1995a).

7.3.3.2 Radiochemistry

During the wet phosphoric acid process, the radionuclides within the phosphate rock are liberated from their host phases and released into solution. The individual radionuclides are partitioned into the phosphoric acid or the phosphogypsum, according

Component	Florida ^a hemihydrate	Florida ^a dihydrate	Australia ^b dihydrate	Iraq ^c dihydrate	Morocco ^d dihydrate	Senegal ^d dihydrate		
	Type of analysis							
	Bulk geochen	nical analysis	Mineral chemical analysis					
CaO	36.9	32.5	32.8	32.94	42.24	33.58		
SO3	50.3	44.0	45.2	44.94	59.85	59.86		
SiO ₂	0.7	0.5	0.21	0.45	0.84	3.49		
Al ₂ O ₃	0.3	0.1	0.17	1.05	0.13	0.28		
Fe ₂ O ₃ total	0.1	0.1	0.02	0.4	<0.07	0.09		
MgO	n.a. ^e	0.1	0.05	0.46	n.a.	n.a.		
P ₂ O ₅	1.5	0.65	0.5	0.18	2.57	0.99		
F	0.8	1.2	1.24	0.6	n.a.	n.a.		
H ₂ O _(crystalline)	9.0	19.0	20.07	19.18	n.a.	n.a.		

Table 7.1. Major element composition (wt.%) of phosphogypsum produced at various phosphoric acid plants

^a Kouloheris (1980).
 ^b Beretka (1980)
 ^c Khalil et al. (1990).
 ^d Martin et al. (1999).
 ^e Not analysed.

Trace element	Phosphate rock source								
	Florida ^a	Florida ^a	Idaho ^a	Tunisia ^a	South Africa ^a	Morocco ^b	Senegal ^b		
Cu	8	n.a.c	10-42	6	103	<6	9		
Pb	3–7	n.a.	3–7	n.a.	n.a.	<18	<11		
Zn	9	n.a.	18-112	315	6	18	6		
Cd	7	9–28	n.a.	40	n.a.	n.a.	n.a.		
Мо	16	n.a.	<1-2	5	n.a.	n.a.	n.a.		
Ni	2	n.a.	3-15	15	13	13	13		
Cr	n.a.	1.5	<10-70	n.a.	n.a.	n.a.	n.a.		
Hg	n.a.	n.a.	n.a.	14	<0.05	n.a.	n.a.		
As	40	0.25	<1-2	n.a.	n.a.	<5	<6		
Sb	100	n.a.	0.3-0.8	n.a.	n.a.	n.a.	n.a.		
Se	n.a.	n.a.	4–67	n.a.	n.a.	n.a.	n.a.		
U	n.a.	18	6-13	n.a.	n.a.	n.a.	n.a.		

Table 7.2. Trace element content (ppm) of phosphogypsum produced at various phosphoric acid plants

^a Rutherford et al. (1994).
^b Martin et al. (1999).
^c Not analysed.

to their solubility (Rutherford et al. 1994). Uranium and thorium radionuclides and Pb-210 concentrate in the phosphoric acid whereas most of the Ra-226 and Po-210 are concentrated in the phosphogypsum. The latter radionuclides are not contained in calcium sulfate crystals but are hosted in separate phases (Jarvis et al. 1994; Rutherford et al. 1994). Radium-226 of the U-238 decay series has a charge (4^+) and ionic radius (0.152 nm) which makes it an unlikely substitution for calcium $(2^+, 0.099 \text{ nm})$ in the calcium sulfate lattice. A proportion of the Ra-226 is associated with extremely finegrained water insoluble particles. The water insoluble phases are possibly barium or strontium sulfates, fluorides, phosphates and/or aluminium phosphates resembling the mineral crandallite (Jarvis et al. 1994; Rutherford et al. 1994; Burnett et al. 1995). The remaining percentage of Ra-226 is likely adsorpted onto organics, associated with colloids, and present in water soluble solids (Burnett et al. 1995). Thus, radionuclides in phosphogypsum are contained in solid crystal lattices and on adsorption sites. In addition, phosphogypsum stacks contain stack fluids in the interstices of the phosphogypsum solids which contain acids, including phosphoric acid. These pore fluids have been observed to be very high in uranium and Pb-210 with moderate concentrations of Ra-226 (Burnett and Elzerman 2001).

Radium-226 activity (about 500 to 2 000 Bq kg⁻¹) is usually the largest source of radioactivity in phosphogypsum although high activities (>1 000 Bq kg⁻¹) of Pb-210 and Po-210 have also been reported (Rutherford et al. 1994). Radium-226 decays to the important radon isotope Rn-222 which is of significant environmental concern (cf. Sec. 6.4.2.2).

7.3.4 Disposal of Phosphogypsum

The amount of phosphogypsum produced by the fertilizer industry on a worldwide basis is in the order of 100 Mt per year (Wissa and Fuleihan 2000). Such large quantities of phosphogypsum create a major disposal problem. Disposal options for this waste are either discharging it into the sea, backfilling it into mined-out open pits, or stacking it in large heaps. In Florida alone, phosphogypsum is generated at a rate of 40 Mt per year, and phosphate mining operations have produced 1000 Mt of stockpiled phosphogypsum covering over 2000 ha of land (Burnett and Elzerman 2001).

7.3.4.1 Marine Disposal

The dumping of phosphogypsum at sea and into rivers has been pursued for many years at various operations around the world. Such a disposal practice has a number of advantages:

- 1. Insoluble mineral particles like quartz settle on the stream or sea bed and become incorporated into marine sediments without any environmental impacts.
- 2. Soluble and sparingly soluble constituents (i.e. calcium sulfate crystals, free phosphoric and sulfuric acids, fluorine compounds, heavy metals, metalloids and radionuclides) are dispersed in a very large volume of water to background concentrations (i.e. dilution is the solution to pollution).
- 3. There is no contamination threat to ground and surface waters on land.

Despite these advantages, the disposal practice may cause elevated phosphate, cadmium and radionuclide levels in coastal seawater, and discharged spoils could end up being dredged and dumped on coastal land. Increased phosphate concentrations stimulate the growth of algae, and cadmium and radionuclides may bioaccumulate in coastal marine life (van der Heijde et al. 1990). Hence, while sea dumping is an effective disposal option, there are question marks about the risks of environmental impact and contaminant transfer into the local foodchain. Nowadays, only a few phosphoric acid plants discharge their phosphogypsum directly into the sea. Furthermore, fertilizer manufacturing plants are rarely situated close to the open sea into which phosphogypsum can be discharged. This leaves land disposal as the only option.

7.3.4.2 Backfilling

Backfilling mined-out open cuts or underground workings with phosphogypsum is a possible disposal option (Wissa and Fuleihan 2000). However, phosphogypsum contains acids in liquid inclusions and pores. This acidity requires that backfilling is based on the blending of phosphogypsum with sufficient acid buffering materials. The phosphatic clays produced during beneficiation may be suitable for blending as they can have a high calcareous content. Mixing these calcareous materials with phosphogypsum can neutralize the acidity remaining in the phosphogypsum (cf. Sec. 2.10.4).

Once backfilling has occurred, the ground water will eventually return, approximating the pre-mining ground water table. If the open pit is not lined with clay or other impermeable liners, the phosphogypsum will become part of the local aquifer (cf. Sec. 4.5). Phosphogypsum is similar to gypsum in its solubility, and phosphogypsum can be host to elevated radionuclide, heavy metal and metalloid concentrations. Consequently, the disposal of phosphogypsum into mining voids may lead to: (*a*) the dissolution of phosphogypsum; (*b*) the mobilization of contaminants; and (*c*) the contamination of ground water with acid, radionuclides, heavy metals, and metalloids. Because of such concerns, phosphogypsum is generally not recommended as backfill (Wissa and Fuleihan 2000).

7.3.4.3 Phosphogypsum Stacks

The most widespread practice in the phosphate industry is to stack the phosphogypsum near the production plant. The use of tailings dams is less frequent. Prior to stacking, the phosphogypsum is filtered and/or washed at the processing plant to remove any soluble phosphate. Two different stacking procedures are employed, wet-stacking and dry-stacking. Dry-stacking is applied in arid areas with limited water supplies. Wet-stacking is the most common method employed and is based on the pumping of the waste slurry, containing about 20 to 25% solids, from the plant to a repository. The phosphogypsum is slurried with process, sea or fresh water and pumped to the top of an impoundment known as stack where a pond-and-pile system is operating (Fig. 7.5). At the top of the stack, the sand- to silt-sized phosphogypsum solids settle. The water is removed from the settling pond and sent to a nearby collection pond. Alternatively, the water is indirectly removed – after it seeps through the stack – and collected in

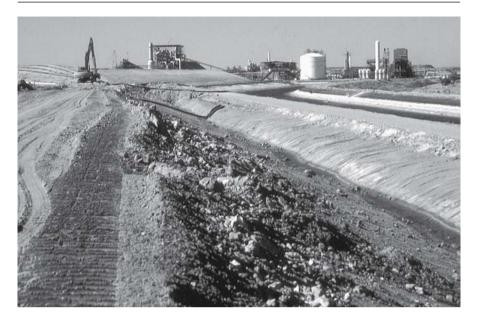


Fig. 7.5. Phosphogypsum stack at the Phosphate Hill mine, Australia. The dry phosphogypsum is reslurried prior to disposal and discharged onto the top of the stack where the solids settle. Waters (pH 1.5) seep through the stack and are collected in circumscribing plastic lined ditches

ditches or ponds that circumscribe the stack (Fig. 7.5). If acidic, phosphatic process water has been used to slurry the phosphogypsum, the process water is usually recycled. If sea water has been used, the process water is discharged into the ocean. The stack grows as the dikes that form the impoundment at the top are built up with phosphogypsum. The phosphogypsum stacks may reach several hundred hectares in size and 100 m in height.

Phosphogypsum stacks may exhibit distinct chemical gradients similar to sulfidic waste rock piles and tailings repositories (cf. Secs. 3.9.1, 4.3.2). It is likely that acidic, aerobic conditions are prevalent in the upper part of the stack. Neutral, anaerobic conditions can be expected to develop near its base. Aged waste material, which has been leached for a considerable period of time, would possess near neutral pH values. These aerobic and anaerobic conditions will influence the mobility of radionuclides.

A proportion of Ra-226 in phosphogypsum is water soluble while the remaining percentage may be sorpted onto organics, associated with colloids, and incorporated into extremely fine-grained water insoluble particles (Burnett et al. 1995). The release of Ra-226 from phosphogypsum solids into stack pore waters is possible. Dissolution of the water insoluble phases may occur under anaerobic conditions at the base of the stack. At the base, sulfate-reducing bacteria may not only interact with the calcium sulfate crystals but also with water insoluble minerals. Under anaerobic conditions and upon bacterial reduction, the Ra-226 is released from the sulfates and becomes available for mobilization. Similarly, the highly toxic Po-210 is highly soluble in reducing environments, may be leached from stack bases, and could migrate into aquifer sys-

tems (Bennett et al. 1995). Thus, it appears that phosphogypsum wastes share common characteristics with uranium mill tailings (cf. Sec. 6.7). Uranium mill tailings and phosphogypsum may exhibit elevated radioactivity levels due to abundant Ra-226, and some of this Ra-226 is hosted by solid phases (possibly sulfates, fluorides, phosphates and/or aluminophosphates). Ra-226 and Po-210 that are contained in sulfates, may be released by sulfate-reducing bacteria into porewaters, and may subsequently be mobilized into ground and surface waters.

In order to prevent ground water contamination, any dry or wet stack of phosphogypsum needs to be constructed with a composite liner (i.e. compacted soil or compacted phosphogypsum with a high density polyethylene membrane) and a leachate collection system (US EPA 1997). Otherwise, process water or trapped liquids within phosphogypsum may be leached during rainfall events, and the ground water can become contaminated with acid, sulfate, phosphate, fluorine, radionuclides, and heavy metals. If a phosphogypsum stack has been constructed on calcareous or clay-rich subsoil or with a clay liner, the fluorine-rich process water may react with the carbonate or clay minerals, causing their alteration and dissolution (Arocena et al. 1995b). The dissolution of these minerals would greatly increase permeability and would lead to the transfer of contaminants into aquifers. Therefore, engineering designs for phosphogypsum waste impoundments advocate plastic liners (US EPA 1997).

Upon closure, the stack should be capped with an impermeable layer because the dissolution of phosphogypsum and the leaching of contaminants from the waste need to be avoided. If closed stacks are left uncapped, the phosphogypsum will dissolve and karst-type features will form in the stack (Wissa and Fuleihan 2000). Phosphatic clays with their long-term acid buffering capacity and alkaline pH may be useful materials for the capping of closed phosphogypsum stacks. In addition, compacted phosphogyp-sum may be suitable capping material. Vegetation can be established directly on the phosphogypsum with or without suitable amendments, including limestone, lime or phosphatic clay (Richardson 1995). These amendments are to raise the phosphogypsum pH and to ameliorate the tendency for crusting and cracking of phosphogypsum. Capping the phosphogypsum with materials, such as phosphate waste rocks or phosphatic clays, not only reduces leaching of contaminants and atmospheric emissions from the stack, it also creates suitable substrates for vegetation.

7.3.4.4 Recycling

Much effort has been put into finding alternative uses for phosphogypsum. These possible uses require either reprocessing (e.g. for the production of sulfur or pure calcium sulfate) or minimal/nil reprocessing for large-scale applications (e.g. in agriculture, mine and landfill reclamation, earthworks and construction) (Korcak 1998; Johnson and Traub 1996).

Reprocessing aims to extract pure elements or pure calcium sulfate solids. For example, sulfur can be obtained for sulfuric acid production, and calcium sulfate can be extracted for building materials (e.g. gypsum plaster, boards, tiles, cement, hydraulic binder, mineralizer, artifical marble, fibre boards, glass, glass-ceramics). Some phosphate rocks contain elevated uranium, yttrium, and/or rare earth element concentrations, and their extraction is possible (Scientific Issue 7.1). However, the recovery of

Scientific Issue 7.1. Recovery of Trace Constituents from Phosphate Rock

Resources within Phosphate Rock

Phosphate rock contains on average 0.015% uranium, 0.035% yttrium, and 0.055% rare earth element oxides (Weterings and Janssen 1985; Habashi and Awadalla 1986). Phosphate rock from carbonatite deposits may contain even higher rare earth element concentrations. About 140 Mt of phosphate rock are treated annually for fertilizer production. In the wet phosphoric acid process, much of the uranium, yttrium and rare earth elements present in the phosphate rock ends up in solution or in the solid phosphogypsum particles. The elements are not extracted and are disposed of with the phosphogypsum waste. In total, approximately 21 000 t of uranium, 49 000 t of yttrium and 77000 t of rare earth element oxides are lost annually to phosphogypsum process waters and solid wastes. The waste of such resources is extreme. The amount of yttrium and rare earth elements around the world is much greater than the annual global production of these elements from other sources.

Recovery of Elements

Extensive research shows that recovery of uranium, thorium, scandium, vanadium, yttrium, and rare earth elements is feasible during the manufacture of phosphoric acid. In fact, commercial recovery of rare earth elements during fertilizer production was formerly undertaken in Finland. Whether the extraction of these trace constituents is economically warranted depends on the element content of the phosphate rock, the phosphoric acid production volume of the acid plant, the processing technique, and the market price of the element (Weterings and Janssen 1985). To date, many of the proposed and validated extraction procedures are too expensive to pursue, and despite considerable research efforts, none of the elements have been recovered. There are over 1000 Mt of phosphogypsum waste stockpiled around the world. These enormous waste stacks could be useful resources of uranium, yttrium, thorium, scandium, vanadium, and rare earth elements in the future.

pure elements or pure calcium sulfate from phosphogypsum is not economically viable at this stage. Phosphogypsum has to compete with mined natural gypsum which is mined at considerably higher purity. Moreover, the use of phosphogypsum as raw material for building purposes can be limited due to residual phosphate, high water content, fine particle size, and inconsistent composition. While these characteristics hinder the use of phosphogypsum in building products, it has been found that compacted phosphogypsum can form a high strength material for road beds, making it a suitable road base material.

Phosphogypsum has the potential to be used as agricultural amendment. Phosphogypsum is particularly useful as an amendment for highly weathered, nutrient-poor soils as well as saline, sodic, acid and calcareous soils (Rutherford et al. 1994). Crop yields and pasture quality have been found to improve on phosphogypsum amended soils. Phosphogypsum application can counter crusting of soils, reducing soil runoff and erosion rates. However, elevated radionuclide (Ra-226, Pa-231, Pb-210, Po-210), fluorine and heavy metal levels as well as contained acid water with dissolved phosphate and heavy metals all represent problems for possible agricultural applications (El-Mrabet et al. 2003). Eutrophication of waterways is possible, and radionuclides, heavy metals, and metalloids may be taken up by plants.

In the United States, radioactivity limits imposed by the US EPA restrict the use of phosphogypsum as building material and soil amendment. If phosphogypsum is used for building and agricultural applications, purification of phosphogypsum may be necessary. Separation of radionuclides, heavy metals and metalloids from phosphogypsum would have to be achieved through chemical or physical means. The distinct chemical and mineralogical properties of different size fractions form the basis of proposed purification procedures. The purification is designed to lower the contaminant load and radioactivity of phosphogypsum. A reduction in contaminant load is possible to some extent through the removal of the finer size fraction which is enriched in radionuclides and heavy metals (Arocena et al. 1995a). Despite the research efforts into alternative uses of phosphogypsum, there are no large-scale applications of phosphogypsum. As a result, the amount of phosphogypsum piled up around the world is steadily increasing.

7.3.5 Potential Hazards and Environmental Impacts

7.3.5.1 Phosphogypsum

The most widespread disposal practice in the phosphate industry is to stack the phosphogypsum near the production plant. Improper phosphogypsum stacking causes most of the environmental impacts of phosphate mining and processing. The principal potential hazards and environmental impacts of phosphogypsum stacks are:

- *Failure of stacks*. In the past, several failures of phosphatic tailings ponds and phosphogypsum stacks and dams have occurred. These failures released wastes into waterways and resulted in damage to the local ecosystem (Table 7.3). Phosphorite deposits are commonly hosted or enclosed by carbonate rocks which are susceptible to chemical weathering, leaching, and karst development. Hence, there is a karst sinkhole potential, and in Florida, for example, an entire phosphogypsum stack collapsed into a karst sinkhole.
- Atmospheric emissions. Phosphogypsum stacks may emit gaseous radon and fluorine compounds (SiF₄, HF) in significant amounts into the atmosphere. While radon emissions from phosphogypsum stacks are generally significantly lower than those of uranium mill tailings (cf. Sec. 6.10.2), the US EPA has set radon exhalation limits for phosphogypsum stacks. Phosphate processing plants may also emit sulfur dioxide, radon, and fluorine compounds (SiF₄, HF) in significant amounts into the atmosphere. The technology exists to limit atmospheric emissions of fluorine from phosphoric acid manufacturing plants to environmentally acceptable levels. Few operations recover fluorine by absorption in water using scrubbers, which would minimize environmental impacts and prevent potential health impacts on workers.
- Ground water and surface water contamination. Discharge of phosphopgypsum into local rivers, seepage of process water from stacks, and leaching of stacks – via rainwater percolating through the heaps – have the potential to contaminate local streams and aquifers. Ground water contamination has occurred at several phosphogypsum stacks where the repositories have not been lined and leachates were not collected. At these sites, ground water has elevated total dissolved solids and conductivity values as well as high acid, phosphate, fluorine, sulfate, heavy metal, metalloid, and

Date	Location	Incident	Release	Impact
14.04.2005	Bangs Lake, Florida	Phosphogypsum stack failure	~65 000 m ³	Spillage into marsh- land; plant death
05.09.2004	Riverview, Florida	Phosphogypsum stack failure	227 000 m ³ of acid liquid	Spillage into local creek
31.12.1998	Huelva, Spain	Dam failure during storm	50 000 m ³ of phospho- gypsum with pH 1.5	Spillage into local river
07.12.1997	Mulberry, Florida	Phosphogypsum stack failure	200 000 m ³ of phos- phogypsum and process water	Spillage into local river; destruction of ecosystem
19.11.1994	Hopewell, Florida	Dam failure	1.9 million m ³ of water from a phosphatic clay pond	Spillage into local wetland and river
02.10.1994	Payne Creek, Florida	Dam failure	6.8 million m ³ of water from a phosphatic clay settling pond	Mostly contained in mine area
October 1994	Fort Meade, Florida	?	76000 m ³ of water	Spillage into local river
June 1994	IMC-Agrico, Florida	Sinkhole opens in phosphogypsum stack	?	?
October 1993	Gibsonton, Florida	?	?	Spillage into local river, fish kill
1988	Riverview, Florida	?	Acidic spill	Spillage into local river, fish kill
03.12.1971	Fort Meade, Florida	Clay pond dam failure	9 million m ³ of phos- phatic clay water	Spillage into local river, fish kill
March 1967	Fort Meade, Florida	Dam failure	250 000 m ³ of phos- phatic clay slimes, 1.8 million m ³ of water	Spillage into local river, fish kill

Table 7.3. Examples of phosphate waste repository failures (WISE Uranium Project 2006, reprinted from*www.wise-uranium.org*, with permission from P. Diehl)

radionuclide concentrations (especially Ra-226, Rn-222, U-238 and Po-210). Polonium-210 is considered to be extremely radiotoxic and has been found well above recommended guidelines in aquifers below Florida phosphate mining areas (Bennett et al. 1995). Elevated TDS and conductivity values with high fluorine, heavy metal, metalloid and radionuclide levels in ground waters can be due to natural water-rock interactions and the natural leaching of undeveloped phosphate resources. Consequently, aquifers in phosphate mining districts can have naturally elevated contaminant loads. For instance, high fluorine concentrations are known to cause health problems in humans obtaining their water supplies from ground water bores in such areas (e.g. Senegal).

 Enhanced radioactivity. High uranium and thorium concentrations in some phosphate rocks lead to significant radioactive decay of radionuclides in process waters, phosphatic clays, and phosphogypsum. In fact, the amount of uranium contained within some phosphate rocks, particularly phosphorite deposits, is so high – several tens to hundreds of parts per million – that uranium can be recovered as a byproduct. Liquid and solid wastes may then emit radioactivity levels high enough to require environmental monitoring and safety measures. Thus, improper disposal practices may lead to enhanced radioactivity levels in soils, sediments and waters surrounding a phosphate plant (Bolivar et al. 1995).

From a radiation perspective, inhalation of dust containing radioactive isotopes, direct external radiation, ingestion of surface water, and inhalation of radon represent possible risks to human health (cf. Sec. 6.10.2). Radionuclides are emitted from phosphate rock mining and processing operations in particulate (e.g. U-238), aqueous (e.g. Ra-226) and gaseous forms (e.g. Rn-222), which primarily cause increased radiation exposures in the work force. Phosphogypsum stacks do not pose a dust hazard, because the phosphogypsum has the tendency to form crusts and active phosphogypsum waste repositories are wet enough to prevent dust generation. Radon emissions are the main risk and therefore, Ra-226 - the parent nuclide of Rn-222 - is of prime concern. During mineral processing and phosphoric acid manufacturing, much of the Ra-226 may be incorporated into the phosphogypsum, which may then contain the bulk of Ra-226 and emit high levels of radiation (several tens of pCi g⁻¹). The emission of Rn-222 and its progeny, from phosphogypsum stacks and phosphoric acid plants, is variable and has attracted US EPA regulatory emission standards since there are perceived radiation risks. Moreover, regulations have been put into place on the maximum permissable radiation levels of phosphogypsum (10 pCi g⁻¹) when used in construction and agriculture. This in turn reduces the recycling potential of phosphogypsum. Some studies have indicated, however, that there is no significant risk to human health as the additional radiation dose from phosphogypsum is minimal in comparison to natural levels and background variations (Rutherford et al. 1994).

7.3.5.2

Waste Rocks and Tailings

Environmental concerns are not exclusively related to phosphogypsum stacks. Waste rocks removed to access the phosphate rock are generally piled up next to the mine and hence, become exposed to atmospheric leaching. The leaching may generate seepages with elevated metal, metalloid or radionuclide concentrations. In some cases, leaching of waste repositories led to the contamination of soils, sediments, waters, plants and aquatic organisms with selenium which in turn caused selenium poisoning in grazing animals (Vance 2000; Hamilton and Buhl 2004).

Beneficiation of phosphate rocks results in the production of tailings, which in some instances are discharged into local rivers and coastal marine settings. At such sites, elevated phosphate, fluorine, metal, cadmium and radionuclide levels are found in sediments, waters and marine organisms including seafood (Gnandi and Tobschall 1999; Gnandi et al. 2006). Increased phosphate concentrations stimulate the growth of algae, and cadmium and radionuclides may bioaccumulate in aquatic life which then enter the foodchain (van der Heijde et al. 1990).

7.4 Summary

The production of potash and other salts principally relies on the mining of evaporitic salt deposits. Mineral processing of potash ores involves flotation of the crushed salt which results in the concentration of the salt minerals and rejection of the gangue phases. Alternatively, dissolution of the entire crude salt occurs by hot aqueous solutions, and various salts are precipitated. Currently mined potassium ores have 8 to 30 wt.% K₂O and consequently, potash mineral processing leads to the rejection of the majority of the mined ore as liquid and solid wastes. The major waste products of potash processing include brines and tailings. Brines may be disposed of by: (*a*) reinjection into deep aquifers below the orebodies; (*b*) discharge into the ocean; (*c*) collection in large ponds and release into local rivers; and (*d*) pumping – with or without the solid residues – back into the underground workings and emplacement as hydraulic backfill. Tailings largely consist of mineral processing salts and rejected primary gangue minerals, including clay minerals, sulfides, carbonates, iron oxides, and numerous evaporative salts. The tailings may be backfilled into underground workings or are stacked near the mine site into large piles.

Phosphate rock is mined from sedimentary and igneous deposits, with phosphorites being the predominantly mined deposit type. The principle mineral of all deposit types is apatite in the form of fluorapatite and/or carbonate fluorapatite. Some phosphate rocks display elevated uranium, thorium, heavy metal, metalloid and rare earth element levels. Abundant nuclides of the U-238, U-235 and Th-232 decay series can cause elevated radioactivity and radon levels of the phosphate rock and waste products.

Mining, beneficiation and hydrometallurgical processing of phosphate rock generate waste rocks, phosphatic clays, phosphogypsum, and spent process waters. In the wet process, the beneficiated phosphate rock is reacted with sulfuric acid to produce phosphoric acid. The product of this chemical reaction is a slurry that consists of phosphoric acid and suspended solid crystals. The solids are removed from the phosphoric acid and are termed "phosphogypsum". The term phosphogypsum is a collective term for a waste mixture, comprising major solid and minor liquid waste components. The solid crystals are mainly calcium sulfate (gypsum or bassanite), minor reaction products, and unreacted phosphate rock particles. The calcium sulfate crystals contain liquid inclusions and process water trapped in the interstices of mineral particles. The chemical composition of phosphogypsum is characterized by variably elevated heavy metal, metalloid and radionuclide concentrations. The material is acid due to the presence of residual phosphoric, sulfuric and fluoride acids. Prolonged leaching of stacked phosphogypsum results in the flushing of trapped acids, metals and metalloids; therefore, aged and leached materials display near neutral pH values.

The amount of phosphogypsum produced on a worldwide basis is in the order of 100 Mt per year, and for every tonne of phosphoric acid produced, there are 3 to 6 t of phosphogypsum generated. These large quantities of phosphogypsum create a major disposal problem. The dumping of phosphogypsum at sea has been pursued for many years around the globe. Today, land disposal has become the dominant disposal option. Backfilling phosphogypsum into mine voids is not recommended since it may

Organization	Web address and description
Florida Institute of Phosphate Research (FIPR)	http://www.fipr.state.fl.us Publications and information on phosphate mining, mine wastes, and mine site rehabilitation
US Environmental Protection Agency (EPA)	http://www.epa.gov/radiation/neshaps/subpartr/index.html http://www.epa.gov/radiation/tenorm/sources.htm Radiation and Radon emission from phosphogypsum stacks
World Information Service on Energy (WISE) – Phosphate tailings	http://www.wise-uranium.org Case studies and information on phosphate mine wastes
International Fertilizer Industry Association (IFA)	http://www.fertilizer.org/ifa/ Publications on fertilizer mining, manufacture, trade, and use

Table 7.4. Web sites covering aspects of phosphate and potash mine wastes

bring about mineral dissolution and associated mobilization of contaminants into local ground waters. The preferred disposal option is the stacking of phosphogypsum in large piles near the production plant. A pond-and-pile system allows the sequential built-up of the solid waste and the recycling of process water. Lining and capping of phosphogypsum stacks limit atmospheric emissions of radon and fluorine, and prevent contamination of ground water by acid, sulfate, phosphate, fluorine, radionuclides, heavy metals, and metalloids.

The ever increasing volume of phosphogypsum has stimulated much research into recycling potentials. Numerous alternative uses have been proposed including the use of phosphogypsum as agricultural amendment, as a source of uranium, yttrium and rare earth elements, and as earthworks, construction and building material. However, elevated radionuclide levels, and inefficient and costly extraction procedures, have so far prevented such alternative uses.

Further information on phosphate and potash mine wastes can be obtained from web sites shown in Table 7.4.