Using the above principles, O'Brien et al. (1987) demonstrated that East Australian nodules underwent two stages: (1) incorporation of U(IV) under dominantly suboxic conditions in the sediment; (2) oxidation of U to U(VI) during exposure and reworking of the phosphorite on the seafloor. Differences between U(IV) contents and $^{234}U/^{238}U$(IV) ratios between buried and exposed nodules were related to the length of time nodules were exposed to oxidising conditions at the sediment/water interface. Uranium-series work, therefore, confirms petrographic, sedimentological and other geochemical studies which indicate the importance of reworking in the development of these (and most other) phosphorites.

Environmental issues

On a world-wide basis, the overwhelming majority (>95%) of the 135 Mt of phosphate rock produced annually is used for fertiliser manufacture (Anon 1993). Consequently, long-term growth will ultimately be driven by human population growth, which is expected to remain at current rates for at least several more years (Brown et al. 1987).

In this section, we address some of the most serious problems which effect the environment during the exploitation of phosphate rock. These problems will include those associated with: (1) the mining process; (2) chemical treatments and procedures associated with conversion of phosphate rock to fertiliser; (3) release of toxic or radioactive elements to the environment as a result of mining or processing. In this review, we will emphasise those problems which relate directly to the chemical nature of phosphorites. Many of the current environmental issue centre on contamination by the impurities, especially radionuclides, contained in phosphogypsum, a by-product of fertiliser manufacture, so particular emphasis will be placed on this topic.

Mining and processing

Since most phosphate mining is of the "open-pit" variety, extremely large quantities of material are moved in the process. This type of mining significantly scars the landscape which may not be returned to its original contours following mining. Overburden, ore, ore concentrate, products and by-products are all moved in one form or the other, most often as a slurry which also consumes significant water resources. During the beneficiation process, the ore is concentrated by a variety of methods, usually including sizing and flotation techniques. This results in the production of extremely fine-grained phosphatic "waste clays", one of the most serious environmental problems of the mining/beneficiation part of the fertiliser cycle. This problem is minimised, of course, for deposits (e.g. the Upper Cretaceous – Eocene of the Tethyan province) where the clay content is volumetrically unimportant.

Waste clays are extremely fine grained, with tremendous surface area, so the settling characteristics are very poor. Without any treatment, these clays require decades to settle from about 5 to 20% solids. In Florida, the artificial ponds used for settling take up a substantial (40–60%) fraction of the mine area. Fortunately, progress has been made recently (McFarlin 1992) with rapid dewatering techniques involving the use of a flocculant and floc collector, which brings the solids content up to 25% within a few minutes. Hopefully, this type of technology will prevent the waste clay situation from getting worse in the fu-

ture, but the problem of the numerous clay-settling ponds which now exist must also be addressed.

The "phosphogypsum" problem

Approximately 70% of phosphate ore mined is initially converted to phosphoric acid, an important intermediate product for the manufacture of soluble 'high analysis' phosphatic fertilisers. The commercial production of phosphoric acid may be achieved by thermal methods, involving the reduction of phosphate rock in an electric furnace, or more commonly, using the so-called "wet-process" where the rock is reacted with sulphuric acid. The combined capacity of existing phosphoric acid plants is so large that the phosphate fertiliser industry is the largest single consumer of sulphuric acid in the world. This process also results in the production of substantial quantities of by-product gypsum known as "phosphogypsum". A simplified chemical reaction may be shown as:

$$Ca_{10}(PO_4)_6 F_2 + 10H_2SO_4 + 20H_2O \rightarrow 10CaSO_4 \cdot 2H_2O + 6H_3PO_4 + 2HF \qquad (6)$$
$$\{phosphate\ rock\} \qquad\qquad\qquad \{phosphogypsum\}$$
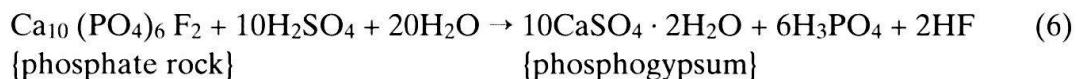
While the mole ratio between gypsum and phosphoric acid is 5 : 3, the mass ratio is about 3 : 1, *i.e.* about 3 tonnes of gypsum are produced for every tonne of phosphoric acid. As a consequence, the phosphate industry as it operates in most parts of the world could more accurately be termed a 'phosphogypsum' industry. Since the phosphate industry measures its phosphoric acid production in terms of many millions of tonnes per year, the amount of by-product gypsum produced is clearly substantial, on the order of 100 Mt yr^{-1} on a world-wide basis.

During wet-process production, $CaSO_4$ may be crystallised in either the dihydrate ($CaSO_4 \cdot 2H_2O$) or hemihydrate ($CaSO_4 \cdot {}^1\!/_2H_2O$) form, depending on the operating conditions. Phosphogypsum produced as a result of this reaction is filtered off and in many areas, including Florida, it is pumped as a slurry containing about 20% solids to a nearby storage area, the so-called "gyp-stacks", where it is cooled and dewatered. The phosphoric acid produced is later reacted with ammonia or concentrated phosphate ore to produce ammonium phosphate or triple superphosphate, the two most common types of phosphate fertilisers.

Phosphogypsum has been used in Japan, Germany and some other countries for production of cement and other construction materials, but its commercial use in the US is currently limited to small quantities sold to farmers as a soil amendment. The US Environmental Protection Agency (EPA) has ruled that gypsum must be placed on stacks or mine cuts, and only limited quantities can be removed for agricultural or research purposes. Phosphogypsum cannot be used for construction or similar applications in the United States subsequent to the June 3, 1992 (57 Fed Reg 23305) EPA ruling. This ruling was predicated on: (1) risk assessments and environmental concerns associated with radionuclides in the ^{238}U decay chain, especially radon (Rn); (2) the US already produces a substantial amount of natural gypsum by mining.

This situation is unfortunate for places such as Florida where the inventory of by-product gypsum has been growing tremendously within the past few decades. This problem does not exist in some countries, such as Morocco, where there are plans to pump

25 kt per day of phosphogypsum from one plant directly into the Atlantic Ocean (Becker 1989). In Florida, it is estimated that more than 600 Mt of phosphogypsum are currently stored at 17 sites throughout the state, with >30 Mt being added each year. At this pace, Florida will have close to 1 Gt of stockpiled phosphogypsum by the year 2000 (May & Sweeney 1982; Nifong 1988).

Besides the obvious waste of a potentially valuable by-product and the unsightly physical appearance of the stockpiles, the main problem associated with phosphogypsum storage is the potential effect on the surrounding environment, specifically the air and water resources in the vicinity of gypsum stacks (Kouloheris 1980). According to a review by Nifong (1988), the principal environmental concerns with phosphogypsum storage are fluoride emissions to the atmosphere and possible contamination of groundwater with radium, sulphate and fluoride, due to leaching by process water or rainwater. Other U-series nuclides associated with phosphogypsum, especially ^{210}Po, have been found at high concentrations in shallow groundwater in the Florida mining area (Harada et al. 1989).

Studies which have considered the radiological aspects of the agricultural use of phosphogypsum have generally concluded that the increased risk relative to more traditional fertilisers is low, both from the increased radon flux from the soil and from uptake by plants (Lindeken & Coles 1978; Lindeken 1980; Roessler 1984, 1988; Mortvedt 1992). The most important pathway between phosphogypsum-derived radionuclides and humans, therefore, is probably through groundwater (Miller & Sutcliffe 1984). Whether the radioactive nuclides are an environmental hazard or not, may be a moot point in terms of use of phosphogypsum in the United States, since a recent EPA ruling has set a 10 pCi g^{-1} limit of ^{226}Ra allowable in phosphogypsum for agricultural purposes. At this stage, it is not at all clear whether radionuclides from phosphogypsum stacks are actually contaminating the surrounding groundwater. Although elevated levels of ^{210}Po have been documented from areas in the vicinity of phosphogypsum stacks in Florida (Burnett et al. 1987; Harada et al. 1989), the source has not been determined. In some cases, it appears that the direct source may be from the natural phosphate rock of the area. In other cases, phosphogypsum appears to be the source.

Research currently in progress concerning the radiochemistry of phosphogypsum has shown that the radionuclides are apparently hosted in a separate phase from the calcium sulphate (Burnett et al. 1992). The radionuclide-bearing phase is insoluble in water and may be an aluminium phosphate with relatively high concentrations of Ba, Sr and REEs. This appears to be somewhat of a paradox. How can radionuclides be leached from phosphogypsum and enter the shallow aquifer when they are contained in a very insoluble phase? The answer may be in the action of bacteria. Cherrier et al. (1995) have shown that bacteria isolated from phosphogypsum seem to incorporate polonium and distribute it into their cellular components in a manner similar to sulphur. In a more recent set of experiments involving leaching of gypsum in columns, it was observed that Po was released when the gypsum was inoculated with sulphate-reducing bacteria (Burnett et al. 1993). These results suggest that sulphur bacteria may cycle Po inadvertently while they are processing sulphur. Both elements are in the same periodic group and have certain chemical similarities. Thus, the enzymatic action of bacteria could be the link which initiates mobilisation of radionuclides from phosphogypsum.

Is there a solution to this problem? Can phosphogypsum be economically purified or converted to a useful form without the associated impurities and put to some good use?

Natural gypsum is mined in several areas of the world and has a variety of uses, especially for construction activities. Unfortunately, phosphogypsum is less suitable for such purposes because of its high water content, fine particle size and generally inconsistent quality. At least two conversion processes are already known: (1) conversion and recovery of sulphur gases which may then be returned to the fertiliser cycle as sulphuric acid; (2) the Merseburg process or double decomposition method, where gypsum is reacted with ammonium carbonate and forms ammonium sulphate, an excellent fertiliser, and by-product calcium carbonate. Unfortunately, the present situation is such that neither process appears to be economically feasible. This is indeed unfortunate, as a potential resource is being wasted and at a great cost, not only in terms of harm to the environment, but in terms of actual expense. Schultz (1992) reported, for example, that if all the gypsum stacks in the United States had to be closed by covering with an impervious membrane and a soil cap to support vegetation, the cost would be in the neighbourhood of US$ 1.3 billion or an average of about $20 million per stack! Furthermore, this cost estimate does not include the on-going costs of environmental monitoring or maintenance. Clearly, it would be in the best interests of everyone involved to pursue options for an environmental-sound yet economically-attractive use of phosphogypsum.

The recent research on the radiochemistry of phosphogypsum mentioned above has shed some insights into this problem. The most important finding is that ^{226}Ra and other radionuclides are not contained in the $CaSO_4$ phase of the gypsum. Although the host has yet to be positively identified (an insoluble phosphate or sulphate appear to be the most likely), the observation that the radionuclide fraction resides in a discrete phase is significant. For example, this finding opens the promise of either physical or chemical separation of the radionuclide fraction from the gypsum component. But can this be done economically? Although the economic outlook does not appear favourable, the new findings provide additional incentive to search for a solution, especially one with a process that will also result in an economically attractive product.

Release of toxic and radioactive elements

Phosphorites may contain relatively high levels of certain elements that may be harmful to humans, either because of some inherent toxicity or because they are radioactive. Of the toxic elements which may be enriched in phosphorites, Cd, Se and As are probably the most important. It should be emphasised, however, that the concentration of these elements varies widely between and sometimes within deposits, so it is important to evaluate each case, on a deposit scale, rather than depend on average analyses. Cadmium in particular can, but does not necessarily (Anon 1989; Johnston & Jones 1992), accumulate in soils and plants through repeated fertiliser use. Japanese law, for example, stipulates a maximum concentration of 1.5 $\mu g\,g^{-1}$ Cd per 1% P_2O_5 (Baechle & Wolstein 1984) in mineral fertilisers, while in Germany and some Scandinavian countries phosphorites containing >20 $\mu g\,g^{-1}$ Cd are considered to be unsuitable for fertiliser production. Sales to Western Europe of phosphate rock from high-Cd deposits such as those of Senegal and Togo have suffered significantly in recent years because of environmental concerns.

Clearly, an understanding of the location and distribution of Cd and other toxic elements, is important in planning the development and beneficiation of a phosphorite deposit. It has been reported that Cd, Pb, Zn, Se, Hg and As may be reduced (volatilised)

considerably by high-temperature calcining of the ore. This is normally uneconomic except in cases where the content of organic matter is high (Isherwood 1992), and also leads to a marked decrease in the chemical reactivity of the phosphorite, reducing the efficiency of the phosphoric acid process. Furthermore, a transference of toxic metals from the fertiliser cycle to the atmosphere, and subsequently to the soil and groundwater in the vicinity of the processing plant, does not necessarily represent a significant improvement to the environmental problem.

During chemical processing, harmful gases may also be released. These include SO_2, associated with the huge quantities of sulphuric acid used by the industry, and fluoride emissions. The technology exists to limit these emissions to environmentally acceptable levels and thus the problem may be limited to ensuring that the regulatory restrictions are being followed. It should also be mentioned in this context that release of potentially harmful elements such as fluoride, may occur without any human intervention at all, i.e. "natural" contamination. This was documented in the case of an unmined area in Senegal where high fluoride levels in the groundwater, presumably leached out of the surrounding phosphate rock, has been implicated as the cause of health problems in the region (Travi 1988).

The one problem that is perceived as being the most important, at least in the United States, is that concerning the content of radioactive elements in phosphorites. Sedimentary phosphorites of most ages and areas (but with some notable exceptions) contain significant uranium concentrations, with typical values over 100 $\mu g\ g^{-1}$. Since virtually all economic deposits of phosphorite are old enough for radioactive equilibrium to be established in the ^{238}U decay chain (this requires approximately 1 Myr), the specific activity (number of radioactive disintegrations per unit time per unit mass) of all U-decay products will be approximately equal. Thus, a Miocene phosphorite from Florida with a U content of 100 $\mu g\ g^{-1}$ will not only have a ^{238}U activity of approximately 33 pCi g^{-1}, but have individual activities of ^{230}Th, ^{226}Ra, ^{222}Rn and other radionuclides of an equivalent amount as well. During mining, and especially during chemical processing of the ore, these radioelements can become separated and radioactive equilibrium is no longer established. This creates an entirely different situation, since each isolated daughter will behave according to its own chemistry and, if truly isolated, will decay away with its own half-life. For example, should ^{210}Po be released into the environment without its radioactive predecessors, it will decay away with its own half-life (138.4 days), rather than being controlled by longer-lived parents.

The major concern in the United States involving the dispersal of radioactive elements associated with phosphate rock, is with the radioactivity of phosphogypsum. This concern, expressed in recent EPA rulings, is centred on the ^{226}Ra content of phosphogypsum, the radioactive parent of gaseous ^{222}Rn. In spite of the fact that emissions from gypsum stacks do not appear to be abnormally high, the concern over any possible contributor to the radon inventory is so great, that the US EPA has greatly restricted the use of phosphogypsum. As mentioned above, new research indicates that radium is apparently hosted in a discrete mineral phase in phosphogypsum, thus opening up the possibility that purification is possible. The problem, and the real challenge, lies in development of an economically feasible way to accomplish this task.