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No. 78

Radiation Protection and Management of NORM Residues in the Phosphate Industry



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RADIATION PROTECTION AND
MANAGEMENT OF NORM RESIDUES
IN THE PHOSPHATE INDUSTRY

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RADIATION PROTECTION AND MANAGEMENT OF NORM RESIDUES IN THE PHOSPHATE INDUSTRY

INTERNATIONAL ATOMIC ENERGY AGENCY
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FOREWORD

The Fundamental Safety Principles (IAEA Safety Standards Series No. SF-1), together with Radiation Protection and Safety of Radiation Sources: International Basic Safety Standards (IAEA Safety Standards Series No. GSR Part 3 (Interim)), set out the principles and basic requirements for radiation protection and safety applicable to all activities involving radiation exposure, including exposure to natural sources of radiation. The Safety Guides on Occupational Radiation Protection in the Mining and Processing of Raw Materials (IAEA Safety Standards Series No. RS-G-1.6) and Management of Radioactive Waste from the Mining and Milling of Ores (IAEA Safety Standards Series No. WS-G-1.2) provide guidance on the control of exposure of workers and members of the public to naturally occurring radioactive material (NORM) in industrial activities involving the exploitation of minerals. This guidance applies irrespective of whether the minerals are exploited for their radioactivity content. The phosphate industry constitutes one of several industry sectors for which the radioactivity content of the minerals and raw materials involved is large enough to warrant consideration by the regulatory body concerning the possible need to control exposures of workers and members of the public.

This Safety Report has been developed as part of the IAEA's programme to provide for the application of its safety standards in the field of radiation, transport and waste safety. It is a compilation of detailed information on the processes and materials involved in the phosphate industry and on the radiological considerations that need to be taken into account by the regulatory body when determining the nature and extent of radiation protection measures to be taken. This is consistent with the graded approach to regulation, in terms of which the application of the requirements of the safety standards is commensurate with the characteristics of the practice or source and with the magnitude and likelihood of the exposures.

This Safety Report was drafted in nine consultants' meetings held between 2002 and 2011. Particular acknowledgement is paid to the contributions made by B.K. Birky, J. Hilton and R. García-Tenorio. The IAEA officers responsible for the preparation of this report were D.G. Wymer and P.P. Haridasan of the Division of Radiation, Transport and Waste Safety.

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1. INTRODUCTION

1.1. BACKGROUND

Phosphorus is an essential component of all living systems, such as nervous tissue, bone and cell protoplasm. Phosphorus is highly reactive and, therefore, is not found as a free element in nature. It occurs principally in rock deposits containing various mineralized forms of calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, from which commercial phosphate, a non-substitutable, non-renewable resource, is derived on a large scale. The production of phosphate fertilizers and animal feeds constitutes the major commercial activity in the phosphate industry. Phosphorus compounds are also used in a wide variety of food, pharmaceutical, industrial and domestic products.

Phosphate deposits contain the naturally occurring radionuclides ^{238}U and ^{232}Th together with their decay progeny, more details of which are given in Appendix I. From the 1950s to the late 1990s, uranium was recovered as a commercial product in some phosphate processing facilities. Regardless of whether or not the ore has potential for uranium recovery, the presence of these radionuclides of natural origin creates a potential need to control exposures of workers and members of the public in accordance with IAEA safety standards (the Standards), in particular the Fundamental Safety Principles [1], Radiation Protection and Safety of Radiation Sources: International Basic Safety Standards (the BSS) [2], the Regulations for the Safe Transport of Radioactive Material [3] and other relevant Safety Guides [4, 5]. In some process materials, the activity concentrations of radionuclides in the ^{238}U decay series are such that, in terms of the Safety Guide on Application of the Concepts of Exclusion, Exemption and Clearance [6], these materials would be considered for inclusion within the scope of regulation, as naturally occurring radioactive material (NORM).

The Safety Report on Assessing the Need for Radiation Protection Measures in Work Involving Minerals and Raw Materials [7] confirms that the phosphate industry constitutes one of several minerals related industry sectors for which some of the processes involved may warrant radiation protection measures through the system of regulatory control for practices. Reference [7] emphasizes the particular relevance of the graded approach to regulation to ensure that any radiation protection measures applied to the industrial processes involved and to the management of NORM residues arising from those processes are commensurate with the characteristics of the operation and with the magnitude and likelihood of the exposures. This implies the need for a thorough understanding of all the processes, the process materials, the associated

radiological risks to workers and to members of the public, and the practicalities of any protective measures that need to be considered.

Radioactivity in phosphate deposits has been a subject of study since the early 1900s, at which time it was already known that phosphate deposits contain uranium in concentrations that can be sufficiently high to be of potential value [8, 9]. The mining of phosphate ore, the processing of it into intermediate and end products and the handling and use of those products can all give rise to exposures of workers and members of the public. Residues associated with phosphate processing may also give rise to exposures. When phosphate rock is digested with acid to produce phosphoric acid (the primary starting point for the manufacture of several major phosphate products), some of the radionuclides, particularly isotopes of radium, become concentrated in residues, such as the scale that tends to form inside pipes and vessels. In high temperature processes, radioactive isotopes of the more volatile elements polonium and, to a lesser extent, lead become concentrated in the fume.¹ Hence, from a radiation protection point of view, process residues are potentially of greater concern than the feedstocks and products.

The production of phosphoric acid, phosphate fertilizer and phosphate animal feed can give rise to risks to human health and to the environment from non-radioactive constituents, notably fluorides and heavy metals, such as arsenic, cadmium, lead and mercury. In sufficient concentrations, fluorides can be toxic and environmentally detrimental. They may have to be removed from phosphoric acid and recovered as fluosilicic acid, which has no significant radioactivity content and is used in such applications as water fluoridation. In some instances, phosphate products may require appropriate management to ensure that the public and the environment are adequately protected against exposure to these non-radiological constituents. Radiological considerations are usually of secondary importance but may also have to be taken into account. A particular example in this regard is phosphogypsum, a co-product of phosphoric acid production that, because of the very large amounts involved, is stored in above-ground engineered containments known as ‘stacks’, often for indefinite periods, or is sometimes disposed of in surface water bodies such as estuaries and the sea. Best practices established for the management of non-radiological risks to humans and to the environment have generally proven to be effective in minimizing any risks arising from the residual radioactivity content. Nevertheless, the radioactivity aspect continues to arouse public concern in some countries.

¹ The term ‘fume’ in this context denotes the vapour and/or suspended fine dust particles released from a high temperature industrial process.

1.2. OBJECTIVE

The objective of this Safety Report is to provide detailed information that will assist regulatory bodies and industry operators in implementing a graded approach to the protection of workers and of members of the public against exposures arising from the processes and products associated with the phosphate industry. The information provided in this Safety Report will also serve as the basis for creating a common understanding, based on common knowledge, between the various stakeholders in the production of phosphate products, including the primary producers (the phosphate industry) and the regulatory bodies involved.

1.3. SCOPE

This Safety Report provides practical information on the radiological risks to workers and to members of the public in the production and use of phosphate based products, their assessment and their management based on the application of the appropriate Standards and good working practices. This information has been compiled from published literature, from unpublished data provided by contributors to this report and from numerous experts with extensive experience, notably in the various sectors of the phosphate industry. The report describes the basic industrial processes associated with the phosphate industry, from the mining of phosphate ore to the production and use of phosphate fertilizers, animal feeds, phosphogypsum and other products. For each process, the radiological parameters of the raw materials, products and residues are quantified, as well as the exposure levels for workers and for members of the public. The data are used as the basis for determining, in principle, the need for, and extent of, regulatory control to ensure that the requirements of the Standards for each aspect of the industrial processes involved are met. Information is provided on monitoring and dose assessment techniques, measures taken to reduce doses, the transport and storage of bulk raw materials and the management of the various waste streams. The report covers both routine operations and non-routine operations such as plant maintenance, decommissioning and decontamination.

1.4. STRUCTURE

Following this introduction, Section 2 provides an overview of the phosphate industry, covering the early history of phosphate fertilizer production, a description of phosphate resources, processes and products and a review of

recent trends worldwide. Section 3 summarizes the radiation protection considerations that apply to NORM industries in general and the phosphate industry in particular, including the application of the Standards, the main exposure pathways involved, the monitoring of exposed workers and dose assessment, as well as providing an example of radionuclide migration during various stages of phosphate processing. Section 4 deals with the mining and beneficiation of phosphate ore, beginning with a description of the processes and process materials involved (including, in particular, the radionuclide concentrations), followed by data on the exposure of workers and members of the public and concluding with a discussion of the regulatory implications. This basic reporting structure — process description, radionuclide concentrations, occupational and public exposure, and regulatory considerations — provides a common framework for the sections that follow, starting with the production of phosphoric acid by acid digestion (Section 5) and then moving on to the manufacture and use of ammonium phosphate fertilizer (Section 6), superphosphate fertilizer (Section 7), nitrophosphate fertilizer (Section 8) and animal feed phosphates (Section 9). The storage, use and disposal of phosphogypsum, a co-product of phosphoric acid production, give rise to a variety of radiological (and non-radiological) considerations, and these are covered in Section 10. The decommissioning of plant and the recycling or disposal of contaminated scrap arising from maintenance or decommissioning are discussed generically in Section 11, the radiological considerations being, in principle, common to all the ‘wet’ chemical processes covered in the preceding sections. Recently, there has been a revival of interest in two additional processes in the phosphate industry that had fallen from favour over the years. These are the extraction of uranium from phosphoric acid, which is addressed in Section 12, and the production of elemental phosphorus by the thermal processing of phosphate rock, which is addressed in Section 13. Additional, more detailed, technical information is presented in six appendices covering the following topics: (i) radionuclides in the ^{238}U and ^{232}Th decay series, (ii) the composition of phosphate ores, (iii) phosphate products and their uses, (iv) the composition of (beneficiated) phosphate rock, (v) methods for converting phosphate rock into phosphoric acid using sulphuric acid attack and (vi) the composition of phosphogypsum. Finally, some additional information is provided in two annexes, one summarizing the particle size characterization of airborne dust in a phosphoric acid plant and related dissolution studies and the other describing the remediation of a coastal and marine phosphate residue deposit.

2. OVERVIEW OF THE PHOSPHATE INDUSTRY

2.1. EARLY PHOSPHATE FERTILIZER PRODUCTION

The production of phosphate fertilizer has always been the primary activity of the phosphate industry and accounts for the vast majority of global phosphate production. Phosphate fertilizer technology was initially very simple. The use of dilute sulphuric acid was introduced to Bohemia in 1831 to convert biogenic phosphate in the form of bones and coprolites² to a largely water soluble form. The product was called superphosphate, a term already used by chemists and apparently first used as early as 1797 by the British physician George Pearson to describe the phosphate compound calcium dihydrogenphosphate ($\text{Ca}(\text{H}_2\text{PO}_4)_2$) found in bone. In 1840, Justus von Liebig made a historic address before the British Association of Science in which he gave a clear exposition of the role of minerals in plant growth and laid the groundwork for modern agricultural science. He was the first to demonstrate scientifically that insoluble phosphates such as bone could be made to release their phosphorus in a form more quickly available to growing plants if they were caused to react with sulphuric acid. That suggestion stimulated John Bennett Lawes to treat coprolites with sulphuric acid and to test the resultant phosphate as a plant nutrient. (Coprolites were a fairly abundant source of phosphorus in the United Kingdom at that time.) In 1842, Lawes was granted a patent on this idea, which permitted him to establish the first commercial superphosphate works. Within 20 years, the United Kingdom was producing 150 000 t of superphosphate per year [10].

In the early stages of the industry, bones from European battlefields, along with cattle bones from the Russian Federation and South America, were popular sources of biogenic phosphates. Surging demand for phosphate led to the extensive export from Peru of guano, a rich source of phosphate. The rapid growth of world demand for phosphate in the 1850s severely depleted these known resources of bones, coprolites and guano [11–13].³ It was the exhaustion of these and other biogenic sources of supply that acted as a catalyst to the emergence of the modern phosphate industry. The supply of phosphate was eventually secured by the discovery of large sedimentary phosphate deposits, known as phosphorite, in South Carolina, United States of America. Mining began in 1867. By 1870, several deposits of phosphorite were being exploited to supply rock to the growing superphosphate industries of Europe and America and

² Coprolites are fossilized animal faeces.

³ By 1851, the United Kingdom was the major importer of bones for bone meal.

bones and coprolites were rapidly supplanted. The estimated market value had grown by that time to some £8 million (1870s values) [14]. By 1889, the South Carolina mine was supplying 90% of the worldwide phosphate industry. At about the same time, prospecting was active in Florida, United States of America, in the search for new sources of commercially exploitable rock [13].

2.2. PHOSPHATE RESOURCES

Phosphate deposits contain calcium and phosphorus, essentially as tricalcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, and fall into five major categories:

- (i) Sedimentary marine deposits;
- (ii) Igneous (magmatic) deposits;
- (iii) Metamorphic deposits;
- (iv) Biogenic deposits, mainly accumulations of bird and bat guano;
- (v) Deposits caused by weathering.

Most phosphate deposits are of a single type, although a few, including some recent discoveries, are mixtures of sedimentary and igneous types. Sedimentary marine deposits account for the majority of worldwide phosphate production [15]. This market dominance is expected to continue in the future. Such deposits originate from the sedimentation of bones of fish and marine mammals and are normally found in layers. Being of animal origin, they commonly contain impurities because non-phosphate components of animal bodies are also deposited with the phosphate-containing portions. Some very old marine deposits are associated with fossils [12]. Igneous deposits, which account for most of the remaining worldwide phosphate production, are created by magmatic extrusion in the form of an alkaline chimney, usually with a roughly circular cross-section, and are relatively inhomogeneous. They tend to contain fewer impurities than sedimentary phosphates and are generally free of organic material.

Phosphate ores contain one or more phosphate minerals suitable for commercial use, such as calcium fluophosphate. The mineralogy of phosphorus rich rocks is complex and there are more than 200 known phosphate minerals. The main mineral group is the apatite group of calcium phosphates having the general chemical formula $\text{Ca}_{10}(\text{PO}_4, \pm \text{CO}_3, \pm \text{OH})_6(\text{OH}, \text{F}, \text{Cl})_2$. The exact chemical composition varies with origin. Apatites are found mainly in sedimentary, metamorphic and igneous rocks and include fluorapatite, hydroxyapatite, carbonate-hydroxyapatite and francolite.

Fluorapatite is described by the chemical formula $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ (alternatively expressed as $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$) or $\text{Ca}_{10}(\text{PO}_4)_6(\text{F},\text{OH})_2$. It is found mainly in igneous and metamorphic environments, such as in carbonatites and mica pyroxenites. Pure fluorapatite contains 42% P_2O_5 .⁴

Hydroxyapatite is described by the chemical formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. It is found mainly in igneous and metamorphic environments but also in biogenic deposits such as bone deposits.

Carbonate-hydroxyapatite is described by the chemical formula $\text{Ca}_{10}(\text{PO}_4, \text{CO}_3)_6(\text{OH})_2$ or $\text{Ca}_{10}(\text{PO}_4)_{6-x}(\text{CO}_3)_x(\text{OH})_{2+x}$. It is found mainly on islands and caves as part of bird and bat excrement (guano).

Francolite is a commonly occurring complex carbonate-fluorapatite that exhibits several kinds of ionic substitution, principally CO_3F^- for PO_4^{3-} (which therefore reduces the phosphate content), Na^+ and Mg^{2+} for Ca^{2+} and perhaps OH^- for F^- [16]. Francolite has been described as two similar but distinct compounds [17] that may be represented in a consolidated form by the chemical formula $\text{Ca}_{10-a-b}\text{Na}_a\text{Mg}_b(\text{PO}_4)_{6-x}(\text{CO}_3)_x\text{F}_y\text{F}_2$ where $a = x-y$ and $x = 0-1.5$. The formula $\text{Ca}_{10-x-y}\text{Na}_{2x}\text{Mg}_y(\text{PO}_4)_{6-z}(\text{CO}_3)_z\text{F}_2\text{F}_{0.5z}$ has also been suggested. Francolite is found mainly in marine sedimentary environments and, to a much lesser extent, in weathered environments such as those covering carbonatites.

2.3. PHOSPHATE PRODUCTION AND RESERVES

Total global phosphate deposits are estimated to be 163 billion t. Most of these deposits are of sedimentary origin, with as little as 4% being of igneous origin [12]. Phosphatic materials are usually characterized in terms of their P_2O_5 content. This is done as a convenience and not as a strict chemical description. Phosphate ores generally have P_2O_5 contents in the range 4–40%. The fluorine content, which is associated principally with fluorapatite and francolite, varies from less than 1% to more than 4% and can be of concern if allowed to find its way into phosphate animal feed products or into the environment. Small amounts of heavy metals, which are potentially harmful to human health, are also found in phosphate ores. More detailed data on the composition of phosphate ores are given in Appendix II.

The concept of exploitability of phosphate deposits is subject to constant redefinition as mining and beneficiation techniques and technologies evolve, partly in response to market forces. A number of economic and technical factors

⁴ Throughout this report, the percentage values used for quantifying chemical composition refer to weight per cent.

influence quite significantly the calculation of phosphate reserves, not least the cost of processing rock with a relatively low phosphate content. For a phosphate deposit to be considered viable, the phosphate mineral component of the ore (that is, the phosphate rock remaining after removal of the barren material) must have a P_2O_5 content above a certain minimum value. The determination of this minimum value tends to be based on the suitability of the phosphate rock for digestion with acid to produce marketable phosphoric acid (the strength of which needs to be at least 28% P_2O_5). Historically, phosphate rock needed to have a minimum P_2O_5 content of 27–30%, but changes in manufacturing practice are now enabling some phosphate deposits to be categorized as ore reserves if the phosphate rock component has a minimum P_2O_5 content of 23% and, in some cases, even less [18]. Owing to the fact that early scientific research into phosphate recovery was conducted on bones, it is still common for the phosphate content of phosphate rock to be expressed in terms of a ‘bone phosphate of lime’ (BPL) number, where a BPL of 1 represents a P_2O_5 concentration of 0.4576%. Thus, phosphate rock with a P_2O_5 content of 30% (a typical value for commercial production of phosphoric acid) has a BPL of 66.

A breakdown of worldwide phosphate production and reserves, as reported in Ref. [19], is given in Table 1. In 2010, China, Morocco and the USA together accounted for almost two thirds of worldwide mining production of phosphate rock. The USA was historically the world’s largest producer but was overtaken by China in 2006–2007. This was symptomatic of a more general trend towards increased phosphate mining outside the USA. At the same time, mining within the USA has been decreasing as a result of the combined effects of pricing policies and local public opposition to mining, especially in Florida, where most of the mining takes place. In 2008, Morocco announced that, in response to surging demand, it was planning to double its mining production, putting it within reach of becoming the future global leader in phosphate mining production.

2.4. PROCESSES AND PRODUCTS

Phosphate ore is converted into commercial products using the following three main process steps:

- (i) After being mined, phosphate ore is beneficiated to produce a concentrate known as phosphate rock (also known as beneficiated phosphate rock or phosphate rock concentrate).
- (ii) According to Ref. [20], as much as 85% of the phosphate rock produced in step (i) is converted into intermediate or final products using a process of

TABLE 1. PRODUCTION AND RESERVES OF PHOSPHATE ROCK (BY COUNTRY) [19]

Country	Estimated mine production in 2010 (million t)	Reserves (million t)
China	65	3700
USA	26.1	1400
Morocco and Western Sahara	26	50 000
Russian Federation	10	1300
Tunisia	7.6	100
Jordan	6	1500
Brazil	5.5	340
Egypt	5	100
Israel	3	180
Syrian Arab Republic	2.8	1800
Australia	2.8	82
South Africa	2.3	1500
Algeria	2	2200
Togo	0.8	60
Canada	0.7	5
Senegal	0.65	180
Other countries	9.5	620
Total (rounded)	176	65 000

acid digestion known as the ‘wet process’.⁵ A relatively small amount is converted directly into elemental phosphorus by reduction in an electric arc furnace in a process known as the ‘thermal process’. It is estimated that 71% of all phosphate rock produced is processed into phosphoric acid

⁵ In some instances, finely ground phosphate rock, sometimes known as ‘reactive phosphate rock’, is applied directly to soil as a fertilizer, while ‘partially acidulated phosphate rock’ has been used in Australia and New Zealand, as well as in some developing countries where plant nutrient resources may be both scarce and unaffordable. It is estimated that the phosphate rock used in this manner accounts for only 0.3% of total phosphate rock production [21–23].

(involving, in most cases, the co-production of large amounts of phosphogypsum), 24% is processed directly into fertilizer (as opposed to indirect processing via phosphoric acid) and the remaining 5% is converted directly into various other products. The annual production of P_2O_5 in the form of phosphoric acid is more than 30 million t.

- (iii) Most of the phosphoric acid produced in step (ii) (estimates vary from 75% to 90%) is subjected to further chemical processing to convert it into fertilizer. The fertilizer products so derived from phosphoric acid thus account for some 55–60% of total phosphate rock production. Of the remaining 10–25% of phosphoric acid produced in step (ii), about half is processed into animal feed supplements and half into a variety of other products. The recovery of uranium from phosphoric acid (to which most of the uranium in the ore migrates) was an important activity prior to the slump in world uranium prices in the 1980s and 1990s. With the revival of interest in nuclear power and the depletion of uranium stockpiles, the recovery of uranium from phosphoric acid is set to increase once more.

An aerial view of a complete phosphate fertilizer production facility is shown in Fig. 1. The site illustrates many of the important social and environmental issues associated with such facilities. It is an environmentally sensitive area, close to a growing urban settlement that is gradually encroaching on the site. The facility has been in operation for over 50 years and now includes land recovered from the stockpiling of phosphogypsum. As part of the long term decommissioning process, this land is planned for redesignation as an amenity for the local community. In preparation for release, it has already been successfully replanted with selected native trees and shrubs.

A schematic view of the processes and products involved in the phosphate industry is shown in Fig. 2. An estimate of how the phosphate in the ore (expressed as P_2O_5) is distributed among the various process materials and products is given in Table 2. The amounts have been calculated by piecing together information from various sources and assuming, as a starting point, an annual phosphate rock production of 160 million t with an average P_2O_5 content of about 30% (66 BPL). Owing to changing circumstances and incomplete commercial data, Table 2 conveys only a general impression and is not intended to be definitive. Nevertheless, it can be concluded that some 80% of all exploitable P_2O_5 currently being extracted from the earth by phosphate mining is destined for use in fertilizer, while about 7% ends up in animal feed supplements. The remainder finds its way into a wide variety of products used in the food and beverage industry, in pharmaceutical and household products and in a diversity of industrial applications including:



FIG. 1. A facility at Huelva, Spain, producing phosphate fertilizer from phosphate rock imported by sea. The associated phosphogypsum stockpiles (stacks) are visible in the background (courtesy: Fertiberia, Spain).

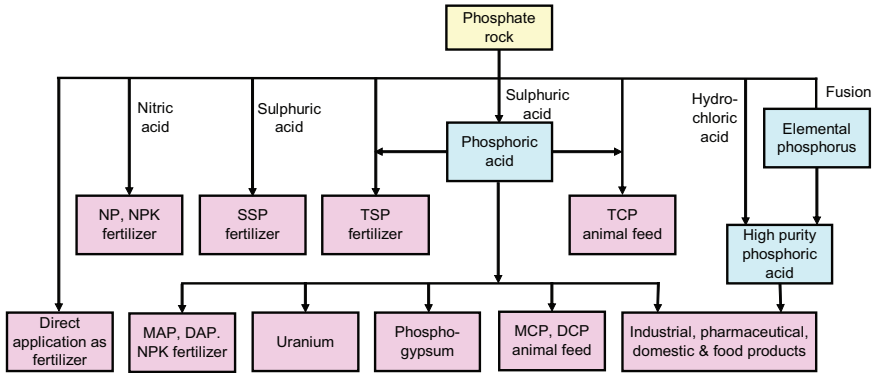


FIG. 2. Phosphate rock product streams. (NP: nitrogen–phosphorus; NPK: nitrogen–phosphorus–potassium; SSP: single superphosphate; TCP: tricalcium phosphate; TSP: triple superphosphate; MAP: monoammonium phosphate; DAP: diammonium phosphate; MCP: monocalcium phosphate; DCP: dicalcium phosphate)

TABLE 2. DISTRIBUTION OF THE PHOSPHATE CONTENT OF THE ORE AMONG THE VARIOUS PROCESS MATERIALS AND END PRODUCTS

Material	Estimated amount of material generated annually worldwide (million t)		Exploitable P_2O_5 content as a proportion of that contained in the ore (%)
	Material mass	Mass of exploitable P_2O_5 content	
Ore ^a	530	48	100
Phosphate rock ^a	160	48	100
Tailings	370	0	0
Phosphogypsum	170	1.8	4
DAP fertilizer	41	20	41
MAP fertilizer	8	4.3	9
SSP fertilizer	23	6	13
TSP fertilizer	6	3.4	7
Other fertilizer	—	4.5	9
MCP–DCP animal feed	6	2.7	6
TCP animal feed	1	0.3	1
Other phosphate products	—	5	10

^a It is recognized that there are significant deficiencies in the extraction of the exploitable content of the rock, leading to estimated losses of up to 30% of the P_2O_5 in the ore prior to beneficiation [24]. For the purposes of this table, these losses are not taken into account.

- (a) The manufacture of chemicals, textiles, leather, glass, cement, ceramics, paper, rubber, electronic components and fire retardants;
- (b) The treatment and coating of metals;
- (c) Foundries;
- (d) Water treatment;
- (e) Mining and oil well drilling.

Many products comprise phosphates of sodium, potassium, calcium, ammonium and magnesium. A more detailed list of the various products associated with the phosphate industry is given in Appendix II. Products destined for human consumption via food, beverages or pharmaceutical products are required to meet strict purity requirements that limit the concentrations of heavy metals and fluoride, thereby ensuring also that radioactivity levels are well below

levels of concern. An analysis of a typical product for human consumption (tricalcium phosphate) showed that the radionuclide concentrations were less than 0.05 Bq/g [25]. Consequently, such products are not discussed further in this report.

2.5. RECENT DEVELOPMENTS AFFECTING THE INDUSTRY

Since 2000, a period of intense change has occurred in the phosphate industry. Traditional European centres of manufacture such as those in Greece, Italy and Spain are progressively closing their plants, with a consequential shift of emphasis in regulatory attention from production operations to the management of legacy issues [26–28]. Countries with emerging economies such as Brazil, China and India have markedly increased their demand for fertilizers in general, and phosphates in particular, for food production [29]. Brazil is importing increased amounts of phosphate fertilizer because its production capacity, although growing, is not keeping pace with domestic demand. China, by contrast, has changed from being a net importer to a net exporter as major new capacity has come on stream [20]. India is almost completely reliant on imported phosphates, but does have some low grade phosphate deposits that may be exploited in the future because of their uranium content [30]. New plants are being planned or built in various parts of the world:

- (a) In Saudi Arabia, a major new facility at Ma'aden will, in future, become one of the world's single largest production sites.
- (b) In Morocco, additional capacity and new joint ventures are being established at Jorf Lasfar, which is set to remain the world's single largest production site for phosphoric acid.
- (c) New facilities and extensions to existing capacity are being constructed in many countries, including Algeria, Brazil, China, Egypt, Jordan, Lebanon and the Syrian Arab Republic.
- (d) Malawi intends to establish its own phosphoric acid production capability and many other countries are considering entering the market [29].

Such changes have shifted the centre of gravity of the industry away from countries with developed economies, resulting in decreased production levels and fewer facilities in those countries. The shift is towards countries with emerging and developing economies, where expansion of production capacity is more than offsetting the decrease in production elsewhere. At the same time, some major phosphate rock producing countries such as Morocco are now committed to the introduction of 'value added' activities such as chemical processing and

granulation, leading to a change in their trading patterns from the mining and shipping of phosphate rock to the production and sale of end products in the form of fertilizer and animal feed. The changes have also brought new challenges for those tasked with maintaining safety standards and best practices in the phosphate industry at both national and international levels [31, 32]. For instance:

- (a) The transport and use of phosphate products across geographical and regulatory boundaries are increasing.
- (b) Phosphoric acid plants that have ceased production have to be decommissioned.
- (c) Neglected or abandoned phosphogypsum stacks have to be reincorporated into a formal management process, which may include finding suitable uses for the material to minimize the amount that has to remain in storage on-site.

Three major new factors in world fertilizer markets as a whole are the projected 70% increase in demand for food by 2050 to feed the growing population, the emergence of a demand for biofuels derived from corn and sugar cane and the surge in demand for animal protein. The demands are growing rapidly, with as yet unknown consequences for patterns of fertilizer consumption. In the USA, a political emphasis on renewable sources of energy, notably biofuels, is having a significant impact on the situation.

In addition, wider sustainability objectives such as those associated with greenhouse gas emissions and the conservation of scarce or non-renewable resources are creating a framework within which the historical role of phosphogypsum as a co-product of phosphoric acid production, rather than as a waste, is being reinvigorated. From the outset, phosphogypsum has been an item of commerce in many countries, with a well-established market value in a variety of applications, especially those in agriculture and construction that have the capacity to consume large volumes [33]. In some markets, however, the commercial use of phosphogypsum has been restricted because of concerns about its radioactivity content and, to a lesser extent, its heavy metals content, even though such concerns appear to be without scientific foundation. In the light of the recent global developments described here, the reasons for treating phosphogypsum as a co-product rather than as a waste become more compelling than ever.

3. GENERAL RADIATION PROTECTION CONSIDERATIONS

3.1. APPLICATION OF THE STANDARDS TO INDUSTRIAL ACTIVITIES INVOLVING EXPOSURE TO NATURAL SOURCES

3.1.1. Scope of regulation

Paragraph 3.4 of the BSS [2] states that exposure to natural sources is generally considered as an existing exposure situation, meaning that the exposure does not fall within the scope of regulation in terms of the requirements for planned exposure situations. However, some industrial activities giving rise to exposure to natural sources have the characteristics of practices and para. 3.4 of the BSS makes provision for the requirements for planned exposure situations to apply in such cases, depending principally on the activity concentrations of radionuclides of natural origin in the material giving rise to the exposure (in this case, any of the process materials involved). The requirements for planned exposure situations apply if the activity concentration of any radionuclide in the uranium or thorium decay chains is greater than 1 Bq/g or the activity concentration of ^{40}K is greater than 10 Bq/g. As a result of this criterion, the phosphate industry is identified in Ref. [7] as being among those industrial activities that are likely to be subject to the requirements for planned exposure situations.⁶

It is important to note that the use of commodities containing radionuclides of natural origin, such as fertilizer, soil amendments and construction materials, is always subject to the requirements for existing exposure situations, regardless of the activity concentrations.

⁶ These criteria do not apply to radon, existing residues in the environment and commodities such as foodstuffs, drinking water, agricultural fertilizer and soil amendments and construction materials, which are normally treated as existing exposure situations regardless of the activity concentrations of the radionuclides concerned, nor do they apply to material in transport, the criteria for which are specified separately in the Standards (see Section 3.1.3). Exposure of workers to radon is regulated according to the requirements for planned exposure situations if the radon concentration in the workplace remains above the applicable reference level after the implementation of remedial action.

3.1.2. Graded approach to regulation

Where the activity concentration values specified in Section 3.1.1 are exceeded, a graded approach to regulation as a practice is adopted in accordance with the requirements of the BSS (para. 3.6). The application of the graded approach to the regulation of operations involving exposure to NORM is described in Refs [4, 7] and is summarized in Sections 3.1.2.1–3.1.2.3.

3.1.2.1. Initial assessment

An initial assessment is made of the process, the materials involved and the associated exposures. For industries engaged in the processing of NORM, the exposure pathways to workers and to members of the public that are most likely to require consideration are those involving external exposure to gamma radiation emitted from process material and internal exposure via the inhalation of radionuclides in dust⁷. Consideration of internal exposure via the inhalation of ²²²Rn and/or ²²⁰Rn emitted from process material (leading to exposure to the short lived progeny of these radionuclides) may also be necessary during the exploitation of certain minerals. Internal exposure via ingestion may need to be considered for members of the public (mainly as a result of water pathways) but is unlikely to be of concern for workers under normal operational circumstances.

The assessment of the effective dose received by an individual involves summing the personal dose equivalent from external exposure to gamma radiation over a specified period and the committed equivalent dose or committed effective dose, as appropriate, from intakes of radionuclides over the same period. The assessment method is described in more detail in Ref. [4].

3.1.2.2. Regulatory options

The four basic options open to the regulatory body, in ascending order of degree of control, are as follows:

The regulatory body may decide that the optimum regulatory option is not to apply regulatory requirements to the legal person responsible for the practice. The mechanism for giving effect to such a decision could take the form of an exemption. For exposure to NORM, the exemption criterion given in the BSS [2] is a dose of the order of 1 mSv per year. The background to this criterion is given in Ref. [34], which concludes that exemption is likely to be the optimum option if the material does not give rise to an annual effective dose received by a worker

⁷ Dust includes aerosols containing solid and/or liquid particles suspended in air.

exceeding about 1–2 mSv (this being a small fraction of the occupational dose limit), bearing in mind that the dose received by a member of the public in such circumstances is likely to be lower by at least an order of magnitude [7].

Where the regulatory body has determined that exemption is not the optimum option, the minimum requirement is for the legal person to submit a formal notification to the regulatory body of the intention to carry out the practice. As in the case of a decision to grant an exemption, this is an appropriate option when the maximum annual effective dose is a small fraction of the applicable dose limit, but it provides the added reassurance that the regulatory body remains informed of all such practices and of any changes to such practices that might have significant radiological implications.

Where the level of exposure to NORM is such that neither exemption nor the minimum regulatory requirement of notification is the optimum regulatory option, the regulatory body may decide that the legal person has to meet additional (but limited) obligations to ensure that exposed individuals are adequately protected. These obligations would typically involve measures to keep exposures under review and to ensure that the working conditions are such that exposures remain moderate, with little likelihood of doses approaching or exceeding the dose limit.⁸ The mechanism for imposing such obligations on the legal person is the granting of an authorization in the form of a registration [4].

Where an acceptable level of protection can only be ensured through the enforcement of more stringent exposure control measures, an authorization in the form of a licence may be required [4]. This is the highest level of the graded approach to regulation and its use for practices involving exposure to NORM is likely to be limited to operations involving substantial quantities of material with very high radionuclide activity concentrations.

3.1.2.3. Control measures for authorized practices

A detailed account of the control measures that may be appropriate for authorized practices involving work with minerals and raw materials is given in Refs [4, 5]. In terms of the graded approach to regulation, the nature and extent of such measures will be commensurate with the type of practice and the levels of exposure, but will generally entail the establishment of some form of radiation protection programme with suitable provisions for monitoring and dose assessment at a more detailed level than in the initial assessment referred to in Section 3.1.2.1.

⁸ For situations in which workers are exposed to gamma radiation and radionuclides in inhaled dust, Ref. [34] states that “Control, if considered necessary, would include the use of methods to suppress or contain any airborne dusts and general radiological supervision”.

Specific radiological measures in the workplace, such as control of the occupancy period or even shielding, may sometimes be appropriate to minimize external exposure to NORM. Materials with relatively low activity concentrations give rise to modest gamma dose rates (typically no more than a few microsieverts per hour), even on contact. In such cases, discouraging access, for example by storing materials in mostly unoccupied areas, may be sufficient. In areas containing materials with relatively high activity concentrations, physical barriers and warning signs may be necessary.

Exposure to airborne dust is likely to be controlled already in many workplaces through general occupational health and safety (OHS) regulations. Control of air quality for the purpose of minimizing dust levels may also help to reduce radon and thoron concentrations. Therefore, the extent to which existing OHS control measures are effective in minimizing workers' radiation exposure is something that the regulatory body would first need to establish before deciding to impose additional control measures for purely radiological reasons. In some workplaces, existing OHS control measures alone may provide sufficient protection against internal exposure. In other workplaces, additional control measures specifically for radiation protection purposes may become necessary for achieving compliance with the Standards. Engineered controls are the favoured option, with working procedures and, finally, protective respiratory equipment being considered only where further engineering controls are not effective or practicable.

Complete containment of material is often impractical, especially where large quantities of low activity concentration materials are involved and spills and the spread of materials outside the area are often of no radiological significance unless substantial and persistent airborne dust levels result. Prevention of resuspension of dust is, therefore, likely to be the most effective approach. Specific measures to control surface contamination only become meaningful where materials with higher activity concentrations are present.

Worker awareness and training are particularly important for supporting the introduction of local rules and for creating an understanding of the precautions embodied in such rules. The work practices of individual employees may exacerbate dust generation and, in some cases, may completely negate the effect of any engineering controls installed. There may be deficiencies in the way in which equipment maintenance tasks are undertaken, implying the need for periodic review to determine if improvements are possible. The general standard of 'housekeeping' and spillage control also needs to be kept under regular review. Even where the materials being handled have a low activity concentration, a reasonable standard of housekeeping may be necessary to ensure that dust resuspension is adequately controlled.

3.1.3. Material in transport

3.1.3.1. Basic criteria

The safety requirements for material in transport are set out in the Regulations for the Safe Transport of Radioactive Material (the Transport Regulations) [3]. The transport of material in its natural or processed state, associated with the phosphate industry, may or may not fall within the scope of the Transport Regulations, depending on the activity concentration of the material.

The Transport Regulations only apply if the activity concentration of the material exceeds 10 times the activity concentration for exempt material.⁹ For individual radionuclides of natural origin, the activity concentrations for exempt material are shown in Table 3.

3.1.3.2. Mixtures of radionuclides

For mixtures of radionuclides, the activity concentration for exempt material is:

$$X_m = \frac{1}{\sum_i \frac{f(i)}{X(i)}} \quad (1)$$

where

X_m is the activity concentration for exempt material (in Bq/g);
 $f(i)$ is the fraction of activity concentration of radionuclide i in the mixture;
 $X(i)$ is the activity concentration for exempt material for radionuclide i
(in Bq/g);

and the condition for application of the Transport Regulations (see Section 3.1.3.1) is:

⁹ This activity concentration criterion applies only to material containing radionuclides of natural origin that is either in its natural state or has been processed only for purposes other than for the extraction of the radionuclides, and that is not intended to be processed for the use of these radionuclides.

TABLE 3. ACTIVITY CONCENTRATIONS FOR EXEMPT MATERIAL IN TRANSPORT

Nuclide	Activity concentration (Bq/g)	Progeny included in secular equilibrium
<i>U-238 decay series</i>		
U _{nat} (U-238)	1	Th-234, Pa-234m, U-234, Th-230, Ra-226, Rn-222, Po-218, Pb-214, Bi-214, Po-214, Pb-210, Bi-210, Po-210
U-238	10	Th-234, Pa-234m
Th-234	1000	Pa-234m
U-234	10, 100 ^a	None
Th-230	1	None
Ra-226	10	Rn-222, Po-218, Pb-214, Bi-214, Po-214, Pb-210, Bi-210, Po-210
Pb-210	10	Bi-210, Po-210
Po-210	10	None
<i>Th-232 decay series</i>		
Th _{nat} (Th-232)	1	Ra-228, Ac-228, Th-228, Ra-224, Rn-220, Po-216, Pb-212, Bi-212, Tl-208 (0.36), Po-212 (0.64)
Th-232	10	None
Ra-228	10	Ac-228
Th-228	1	Ra-224, Rn-220, Po-216, Pb-212, Bi-212, Tl-208 (0.36), Po-212 (0.64)
Ra-224	10	Rn-220, Po-216, Pb-212, Bi-212, Tl-208 (0.36), Po-212 (0.64)
K-40	100	None

^a The applicable value depends on the chemical form of the material.

$$\sum_i x(i) > 10X_m \tag{2}$$

where $x(i)$ is the activity concentration of radionuclide i in the mixture.

Combining Eqs (1) and (2) and making the substitution:

$$f(i) = \frac{x(i)}{\sum_i x(i)} \quad (3)$$

gives the condition for application of the Transport Regulations as:

$$\sum_i \frac{x(i)}{X(i)} > 10 \quad (4)$$

3.1.3.3. *Material with decay chains in equilibrium*

For material in which the radionuclides in each decay series are (or are deemed to be) in equilibrium, the values of activity concentration for exempt material for U_{nat} , Th_{nat} and ^{40}K (see Table 3) can be used to derive the condition for application of the Transport Regulations, with the progeny of ^{238}U and ^{232}Th automatically being taken into account. Equation (4) then becomes:

$$\frac{x(U_{nat})}{1} + \frac{x(Th_{nat})}{1} + \frac{x(^{40}K)}{100} > 10 \quad (5)$$

For materials that are not particularly rich in potassium, Eq. (5) can be approximated to:

$$x(U_{nat}) + x(Th_{nat}) > 10 \quad (6)$$

3.1.3.4. *Material with decay chain segments in equilibrium*

The available data on the radionuclide composition of the material may indicate that equilibrium conditions do not prevail throughout the decay chains but that it may be possible to treat the material as a mixture of decay chain segments, each of which can be assumed to be in equilibrium. In such cases, however, the available data and/or the information in Table 3 may not always be sufficiently detailed to determine unequivocally whether the Transport Regulations apply, in which case a conservative estimate may have to be made by assigning the highest individual radionuclide activity concentration in each decay chain or chain segment to all radionuclides in that decay chain or chain segment. Further information on how to proceed when insufficient data are available on

individual radionuclide activity concentrations is given in the Transport Regulations.

3.2. EXPOSURE TO GAMMA RADIATION

The main radionuclides contributing to gamma exposure are ^{214}Pb and ^{214}Bi from the ^{238}U decay series and ^{228}Ac , ^{212}Pb and ^{208}Tl from the ^{232}Th decay series. The highest gamma energy (2614 keV) is associated with ^{208}Tl . In the phosphate industry, exposure to gamma radiation from radionuclides in the ^{238}U decay series is the main concern for radiation protection and, as in many other NORM industries, arises mainly from accumulations of mineral concentrates or residues. Dose rates are generally highest near process tanks, piping, filters and large material stockpiles. For workers, workplace monitoring or individual monitoring techniques, or a combination of both, are used.

3.3. EXPOSURE TO RADIONUCLIDES IN INHALED DUST PARTICLES

Airborne dust particles arise from the resuspension of dust that has settled on floors and other surfaces, releases from processing operations and the conveying of minerals. For inhalation of such particles by workers in the phosphate industry, exposure to various radionuclides in the ^{238}U decay series (see Appendix I) and to ^{227}Ac in the ^{235}U decay series is the main concern for radiation protection. In situations where the radionuclide activity concentrations in the materials being handled are moderate, it is important to recognize that the silica content of the airborne dust is likely to be of greater concern for occupational health than the radionuclide content.

3.3.1. Particle size

In the absence of particle size information specific to the workplace concerned, an activity median aerodynamic diameter (AMAD) of 5 μm is normally recommended for airborne dust in the workplace [35] and this could be an appropriate value to use in any initial assessment (see Section 3.1.2.1). However, when subsequently performing a more detailed assessment (see Section 3.1.2.3), measurements may indicate that in some workplaces a higher AMAD (e.g. 10 μm) may be more appropriate.

Where high temperature processes are involved, some radionuclides, notably ^{210}Pb and ^{210}Po , can become volatilized in the furnace fume. In the absence of particle size information, an AMAD of 1 μm is normally

recommended in situations where this fume contaminates the air in the workplace (in the area around the furnace, for instance). In high temperature processes in the phosphate industry, however, a higher AMAD may be appropriate and the best approach is to determine the particle size distribution for the particular workplace concerned.

3.3.2. Monitoring techniques for workers

In the phosphate industry, as with other NORM industries, routine determination of intakes of radionuclides by workers is, in most cases, achieved using techniques based on air sampling. This approach is consistent with the findings of an investigation into monitoring strategies and methods for optimization of internal exposures of workers exposed to NORM carried out for the European Commission [36]. One of the conclusions of that investigation was that “Air sampling, rather than biological sampling (or whole body counting) is the best way of assessing doses and providing ALARA information”.

Guidance on the use of techniques based on air sampling for the monitoring of workers is given in Ref. [4]. Such techniques involve the drawing of air through a filter to capture the dust particles, which are then analysed by measuring the activities of alpha emitting radionuclides in the uranium and thorium decay series. The use of these gross alpha activity measurements to determine the intake is subject to the following considerations:

- (a) In materials that have not been chemically processed, the equilibrium of the uranium and thorium decay chains is unlikely to be significantly disturbed, allowing equilibrium to be generally assumed for freshly generated airborne dust particles. However, as discussed in the Annex to Ref. [4], some radon and thoron may have escaped from the dust particles when they are analysed in the laboratory after a delay of some days. The resulting depletion in radon and thoron leads to a corresponding depletion in short lived radon or thoron progeny. For minerals likely to be encountered in the phosphate industry, the retention of radon and thoron can be expected to be in the range 50–100% and it would seem reasonable to assume 75% retention as being typical. On this basis, 1 Bq of ^{238}U captured on the filter corresponds to 7.54 Bq of measured gross alpha activity, while 1 Bq of ^{232}Th corresponds to 5.25 Bq of measured gross alpha activity.
- (b) In materials that have been subject to chemical processing, equilibrium conditions in the airborne dust particles can no longer be assumed and the analysis may have to include the measurement of certain individual decay progeny.

Two basic types of air sampling technique are in use: stationary air sampling (also known as workplace or static air sampling), in which the sampling device remains at a fixed location in the workplace, and personal air sampling, in which the sampling device is attached to the worker in a position such that the air sample is reasonably representative of the air breathed by the worker. The use of stationary air sampling is generally less preferred for dose assessment purposes because the air that is sampled may not be representative of the air breathed by the worker. It is noted in Ref. [36] that the use of stationary air sampling can result in dust inhalation doses being significantly underestimated, sometimes by several orders of magnitude, particularly in workplaces where the resuspension of dust by worker activities is a significant factor. On the other hand, stationary air sampling may result in a significant overestimation of the dose if the worker is not continuously stationed in a dusty area. Three different airborne dust sampling conventions have been established, reflecting different size fractions of the airborne dust particles:

- (i) The inhalable fraction (involving AMADs of up to about 100 μm) includes all airborne particles entering the body through the nose and/or mouth during breathing;
- (ii) The thoracic fraction (involving AMADs of up to about 30 μm) is the sub-fraction of the inhalable fraction that can penetrate into the tracheo-alveolar region of the lung;
- (iii) The respirable fraction (involving AMADs of up to about 10 μm) is the sub-fraction of the inhalable fraction that penetrates into the alveolar region of the lung, including the respiratory bronchioles, the alveolar ducts and sacs.

The selection of the most suitable air sampling device should be based on which dust fraction is to be sampled. A device incorporating an IOM¹⁰ cassette for sampling the inhalable fraction is shown in Fig. 3. The cassette has a 50% sampling efficiency at an AMAD of 40 μm . A sampling device for the thoracic fraction is shown in Fig. 4.

Owing to difficulties in applying personal air sampling to every exposed worker all of the time, monitoring strategies usually involve the assignment of workers to work categories that reflect the general nature and scope of the work activities. In many workplace situations involving exposure to dust containing radionuclides of natural origin, such exposure is not uniform within a work category since a worker may spend time in different exposure environments during the course of the work shift. A further complication arises in accounting for the wearing of respiratory protective equipment.

¹⁰ IOM: Institute of Occupational Medicine, Edinburgh, UK.



FIG. 3. Personal air sampling device for the inhalable dust fraction (courtesy: Thermphos International, Netherlands).



FIG. 4. Personal air sampling device for the thoracic dust fraction (courtesy: Thermphos International, Netherlands).

Air sampling equipment and techniques have been reviewed in terms of their applicability to radiation protection in workplaces involving exposure to radionuclides in airborne dust [36]. Some of the findings of that review are summarized in the following:

- (a) Since air samplers are designed to follow a specific particle size sampling convention based on industrial hygiene sampling criteria, they typically underestimate the true ambient aerosol and thus the activity inhaled. The degree of underestimation depends on the AMAD and geometric standard deviation (GSD) of the particle size distribution of the ambient aerosol and on the type of sampler used. A correction factor can be applied to minimize the degree of underestimation of the airborne activity concentration but this does not remove all of the uncertainty because the AMAD and GSD vary with location, time and circumstances of dust production and can, therefore, never be known precisely.
- (b) The aerosol particle size distribution also has a significant effect on the dose coefficient (the committed effective dose per unit intake of activity), leading to an additional source of uncertainty when assessing the effective dose due to the inhalation of particles. The dependence of the dose coefficient on AMAD is particularly strong for particles of lung absorption class S. When assessing the effective dose, it is important to select a sampler with an efficiency that follows as closely as possible the AMAD dependency of the relevant dose coefficients.
- (c) Knowledge of the lung absorption class is important because it is needed for determining not only the most appropriate dose coefficient but also the type of sampler that best minimizes the errors arising from an incomplete knowledge of the particle size distribution.
- (d) The preferred type of sampling for minimizing dose assessment errors is inhalable sampling for particles in lung absorption class F and thoracic sampling for particles in lung absorption classes M and S. While particles of class M or S are likely to be encountered in many NORM industries, it is pointed out that thoracic samplers are presently not as widely available as inhalable samplers and often are not suitable for alpha counting owing to the dust particles being collected on foam rather than flat filters.
- (e) Where the particle size distribution is not known, the assignment of an AMAD of 5 μm has been found reasonable in minimizing errors in assessing the effective dose, whatever the true value of AMAD, sampling

type, radionuclide and lung absorption class.¹¹ The assignment of a GSD of 2.5 is recommended by the International Commission on Radiological Protection (ICRP) for aerosols with an AMAD greater than 1 µm when the actual value is unknown [37]. For a GSD of 2.5, sampling efficiency correction factors, as referred to in (a), are given in Table 4.

The activity inhaled by workers, as determined from the alpha counting of dust samples collected on filters, may be underestimated if there is significant alpha particle self-absorption in large particles or in multilayers or agglomerates of smaller particles deposited on the filter. In such cases, dust loadings on filters may need to be restricted accordingly [38]. Various types of filter medium and sampling cassette are available. Where the dust concentration is relatively low (say, about 1–2 mg/m³) and sampling is undertaken over a 4–6 h period, the choice of filter medium and cassette is not likely to be critical. However, when the dust concentration is relatively high (more than about 3 mg/m³) and the sampling is undertaken over a period of 8 h or more, the selection of equipment requires more careful consideration. For some types of filter medium, such as PVC, part of the sample may be lost as a result of dust not fully adhering to the surface of the filter. For some types of monitoring cassette, the dust may adhere to the inside wall, requiring it to be removed by washing and added to the material collected on the filter prior to radiometric analysis.

3.3.3. Calculation of effective dose

Dose coefficients (values of committed effective dose per unit intake of activity) for inhalation of radionuclides by workers and members of the public are

TABLE 4. SAMPLING EFFICIENCY CORRECTION FACTORS FOR ESTIMATING THE AIRBORNE ACTIVITY CONCENTRATION OF PARTICLES WITH A GSD OF 2.5 [36]

AMAD (µm)	Correction factor		
	Inhalable sampler	Thoracic sampler	Respirable sampler
1	1.04	1.05	1.11
5	1.18	1.41	2.5
10	1.31	2.1	5.6

¹¹ The measurement of the AMAD requires specialized equipment such as a cascade impactor.

specified in a database compiled by the ICRP [39]. The values are based on the model for the respiratory tract described in Ref. [37]. The dose coefficients for workers quoted in Ref. [39] cover a wide range of AMADs. Most of the values for AMADs of 1 and 5 μm appear also in Table III-2A in Schedule III of the BSS [2]. The dose coefficients for members of the public are specified in Ref. [39] for a default AMAD of 1 μm and also in Table III-2E in Schedule III of the BSS [2].

It is pointed out in Ref. [36] that in most NORM industries, the radioactive components of the material involved, and thus of its aerosol particles, are contained within a matrix of non-radioactive elements and their compounds. These matrices often determine the solubility of the particles and it is, therefore, appropriate in such cases to choose the same lung absorption class for all the radionuclides contained within them. It is further pointed out that many of these materials are resistant to all but the most vigorous forms of chemical attack and that their dust particles are obviously lung absorption class S. This reportedly applies to radium rich process scales of the type likely to be encountered in the phosphate industry. However, lung absorption class S may not be appropriate for materials that have been subjected to vigorous chemical treatment. In such cases, it may be more appropriate to determine the lung absorption class experimentally for the particular material involved.

In high temperature processes, the volatile radionuclides ^{210}Pb and ^{210}Po are likely to be removed from the original mineral matrix. When assessing doses arising from the inhalation of furnace fume and precipitator dust, therefore, the most appropriate lung absorption class needs to be determined experimentally.

Inhalation dose coefficients applicable to workers in industrial operations involving low solubility airborne dust particles are given in Table 5. The coefficients relate to lung absorption class S to the extent possible and cover all radionuclides with significant dose contributions. In the few instances where a value for class S is not available, the value given is that corresponding to the next fastest lung absorption class for which information is available.¹² Most of the values in Table 5 are taken from Ref. [39]. In some cases (denoted by bold figures), values for lung absorption class S are not available from this source and data are quoted instead from the results of other calculations [36, 40] based similarly on the ICRP respiratory tract model described in Ref. [37]. Table 6 sets out the inhalation dose coefficients applicable to workers in industrial operations involving medium solubility airborne dust particles such as those that might occur in chemical processing facilities. The coefficients relate to lung absorption class M and are taken from Ref. [39] or, for those figures in bold, from Ref. [36].

¹² The use of dose coefficients for lung absorption classes other than class S in these few instances may lead to some underestimation of the dose.

TABLE 5. RADIONUCLIDE SPECIFIC INHALATION DOSE COEFFICIENTS FOR WORKERS (LOW SOLUBILITY DUST PARTICLES)

Radionuclide	Dose coefficient for specified AMAD ($\mu\text{Sv/Bq}$) ^a				
	0.3 μm	1 μm	3 μm	5 μm	10 μm
<i>Uranium decay series</i>					
U-238	10	7.3	7.2	5.7	3.5
U-234	12	8.5	8.6	6.8	4.1
Th-230	18	13	10	7.2	5.2
Ra-226	4.4 (M)	8.7	8.7	6.9	4.2
Pb-210	0.76 (F)	5.2	5.3	4.3	2.7
Po-210	3.9 (M)	3.9	3.5	2.7	1.7
Ac-227 (from U-235 series) ^b	88	66	52	47	27
Series in equilibrium ^{b,c}	53.1	49.6	45.7	35.8	22.6
<i>Thorium decay series</i>					
Th-232	32	23	17	12	8.1
Ra-228	3.3 (M)	15	14	11	7.1
Th-228	45	37	33	25	18
Ra-224	3.3 (M)	2.9 (M)	3.1 (M)	2.8	1.3 (M)
Series in equilibrium ^c	83.6	77.9	67.1	50.8	34.5

^a The dose coefficients quoted are those corresponding to lung absorption class S, except where specified in parentheses as M or F. Values shown in bold are taken from Ref. [36] (rounded to two significant figures) or, in the case of ²²⁴Ra, from Ref. [40]. All other values are taken from Ref. [39].

^b The natural abundance of U-235 is 0.711%, resulting in an activity concentration in natural uranium of 0.046 relative to that of U-238. Consequently, the relative contributions to the inhalation dose from the U-235 decay series radionuclides are insignificant except for that from Ac-227. The dose coefficient for Ac-227 is multiplied by 0.046 in calculating the dose coefficient for the full series.

^c The values refer to the dose per unit activity of the parent radionuclide.

Many assessments of worker doses reported for NORM industries are based on the inhalation dose coefficients given in Table III-2A in Schedule III of the BSS [2] for AMADs of 1 or 5 μm , since these coefficients, by international consensus, provide the basis for regulation in accordance with the Standards. However, the BSS do not provide coefficients for ²²⁸Ra, ²²⁴Ra, ²²⁶Ra, ²¹⁰Pb and ²¹⁰Po in lung absorption class S, with the result that, for low solubility particles, the coefficients for class M (or F in the case of ²¹⁰Pb) have to be used instead. For medium solubility particles, the coefficients for lung absorption class F have to be

TABLE 6. RADIONUCLIDE SPECIFIC INHALATION DOSE COEFFICIENTS FOR WORKERS (MEDIUM SOLUBILITY DUST PARTICLES)

Radionuclide	Dose coefficient for specified AMAD ($\mu\text{Sv/Bq}$) ^a				
	0.3 μm	1 μm	3 μm	5 μm	10 μm
<i>Uranium decay series</i>					
U-238	3.8	2.6	2.2	1.6	1.1
U-234	4.4	3.1	2.7	2.1	1.4
Th-230	51	40	35	28	17
Ra-226	4.4	3.2	2.8	2.2	1.5
Pb-210	0.76 (F)	1.0	0.93	0.74	0.45
Po-210	3.9	3.0	2.8	2.2	1.1
Ac-227 (from U-235 series) ^b	260	210	180	150	90
Series in equilibrium ^{b,c}	80.2	62.6	54.7	43.7	26.7
<i>Thorium decay series</i>					
Th-232	54	42	37	29	18
Ra-228	3.3	2.6	2.2	1.7	0.98
Th-228	36	30	28	22	12
Ra-224	3.3	2.9	3.1	2.4	1.3
Series in equilibrium ^c	96.6	77.5	70.3	55.1	32.3

^a The dose coefficients quoted are those corresponding to lung absorption class M, except where specified in parentheses as F. Values shown in bold are taken from Ref. [36] (rounded to two significant figures). All other values are taken from Ref. [39].

^b The natural abundance of U-235 is 0.711%, resulting in an activity concentration in natural uranium of 0.046 relative to that of U-238. Consequently, the relative contributions to the inhalation dose from the U-235 decay series radionuclides are insignificant except for that from Ac-227. The dose coefficient for Ac-227 is multiplied by 0.046 in calculating the dose coefficient for the full series.

^c The values refer to the dose per unit activity of the parent radionuclide.

used for ²¹⁰Pb. In addition, the dose coefficients for ²²⁸Th given in the BSS are different from those incorporated into the ICRP database [39] and given in Tables 5 and 6. For airborne dust particles likely to be encountered in the phosphate industry, the implications of using the BSS coefficients instead of those in Tables 5 and 6 can be estimated from the expected radionuclide solubilities and concentrations in the various process materials. It is found that the implications are significant only for radionuclides of low solubility and depend mainly on the relative concentrations of ²²⁶Ra and its progeny. In summary:

- (a) For particles of phosphate ore, phosphate rock or phosphogypsum, all radionuclides can be assumed to be of low solubility. For phosphate ore and phosphate rock, in which near equilibrium conditions prevail, the use of BSS dose coefficients could lead to an underestimation of the inhalation dose by up to 20%. For phosphogypsum, in which there is a high degree of disequilibrium with a characteristically high ^{226}Ra content, the use of BSS coefficients could lead to a more serious underestimation of up to 40%.
- (b) For particles of fertilizer product, the decay chains are not in equilibrium and the radionuclide solubility could be regarded as either low or medium, depending on the radionuclide (see Section 6.3.2). Since the concentrations of ^{226}Ra and its progeny are characteristically low, the use of BSS dose coefficients will give doses very similar to those calculated using the coefficients in Tables 5 and 6.

The derivation of the dose coefficients for ^{226}Ra specified in the ICRP database [39], the BSS [2] and Tables 5 and 6 is based on the assumption that ^{222}Rn produced in the respiratory tract does not have the same biokinetic behaviour as its parent ^{226}Ra , but rather is removed to the environment at a rate of 100 d^{-1} (see Annex B of Ref. [41]). Should the removal rate be lower than 100 d^{-1} , the use of these dose coefficients would, by implication, result in the dose being underestimated. In an extreme (and highly unlikely) situation of zero radon removal from the respiratory tract, calculations based on data reported in Ref. [36] suggest that the degree of underestimation could be about 50% for particles of phosphate ore, phosphate rock and phosphogypsum and about 10% for particles of fertilizer.

3.4. SELECTIVE MIGRATION OF RADIONUCLIDES

The mining and beneficiation of phosphate ore involves only physical processes and is, therefore, unlikely to affect the equilibrium that generally exists in the ore. However, chemical or thermal processing of phosphate rock will mobilize the ^{238}U and ^{232}Th decay series radionuclides contained in the ore. This causes different radionuclides to migrate in different ways, thus destroying the equilibrium condition. A knowledge of the resulting radionuclide compositions of the various process materials and products is essential for determining the nature of any control measures that might be needed to ensure that the workers and members of the public are adequately protected.

As an illustration of radionuclide migration during the processing of phosphate ore into fertilizer, a mass balance and a radionuclide balance for a wet process facility processing sedimentary rock are shown in Fig. 5. The activity

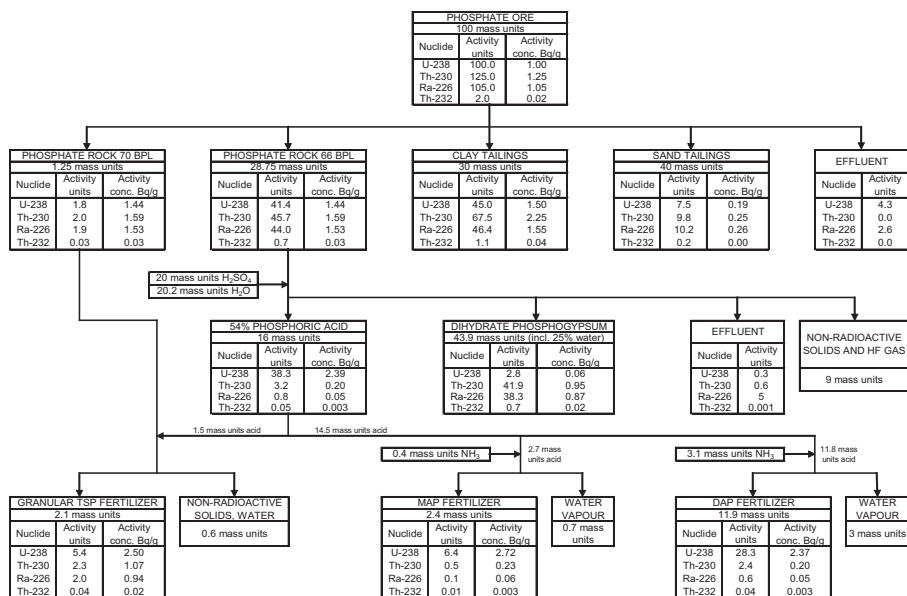


FIG. 5. Typical mass balance and radioactivity balance in the production of phosphate fertilizers in central Florida, USA.

concentrations used in this example are typical of those measured in fertilizer production facilities in central Florida, USA, using local phosphate ore as a feedstock. The relative amounts of the three types of fertilizer shown in Fig. 5 reflect current production patterns. For the production of MAP and DAP fertilizers, phosphate rock with a P_2O_5 content of 30% (66 BPL) is assumed in Fig. 5. This reflects typical historical production values. The exhaustion of high grade rock together with improvements in beneficiation and chemical processing technology has enabled the exploitation of ores with values as low as 24% (52 BPL). During the digestion of the rock with sulphuric acid, the uranium contained within it migrates primarily to the phosphoric acid, whereas most of the radium ends up in the phosphogypsum. The radionuclide composition of the phosphoric acid is, in turn, carried through to the various fertilizer products that are derived directly from it.

4. MINING AND BENEFICIATION OF PHOSPHATE ORE

4.1. PROCESS DESCRIPTION

4.1.1. Mining

Most commercially exploited sedimentary phosphate deposits are located within a few tens of metres of the earth's surface. These deposits are usually mined by opencast techniques, although some underground mining has been carried out in Egypt, Morocco and the Russian Federation. The overburden and phosphate ore are usually removed by large excavating machines such as electrically operated draglines (see Fig. 6), bucket wheel excavators or electric shovels. In smaller operations, wheeled loaders or hydraulic excavators may be used. Sedimentary phosphate ore currently mined in the USA contains sand, clay, fine particles of phosphate and, in the Florida operations, larger phosphate 'pebbles'. A sample of sedimentary ore from central Florida is shown in Fig. 7. In the mining of igneous deposits and some sedimentary deposits, the overburden and/or phosphate ore has to be broken up by drilling and blasting before it can be removed. The overburden may be set aside for future use in the mine remediation



FIG. 6. Dragline (courtesy: Florida Industrial and Phosphate Research Institute).



FIG. 7. Phosphate ore of sedimentary origin.

process or returned directly to the mined-out pit area. In some operations the mined ore is exposed to high pressure water jets, as shown in Fig. 8. This generates a slurry, which is pumped directly to the beneficiation plant through a pipeline, as shown in Fig. 9. In other mining operations, the ore may first have to be loaded into trucks for haulage to a nearby crushing facility, after which the crushed ore is transported to the beneficiation plant by a slurry pipeline, train or conveyor. In some hard rock operations, such as those handling ore of igneous origin, the rock is first crushed and then transported by a conveyor to a wet or dry milling facility, after which the milled ore is transported to the beneficiation plant by a slurry pipeline.

4.1.2. Beneficiation

A typical beneficiation process for sedimentary rock is shown schematically in Fig. 10. The first step is usually a wet screening operation (‘washing’) designed to clean and separate the larger phosphate particles from the slurry and to disintegrate mechanically the large balls of clay. The equipment used may include vibrating and stationary screens as well as log washers, hydrocyclones and clay disintegrators. In operations in Florida, USA, phosphate pebbles (see Fig. 11) are screened out from the clay, sand and sand sized phosphate rock, moved to dewatering tanks and stockpiled by conveyors for



FIG. 8. High pressure water jets (courtesy: Florida Industrial and Phosphate Research Institute).



FIG. 9. Slurry pipeline (courtesy: Florida Industrial and Phosphate Research Institute).

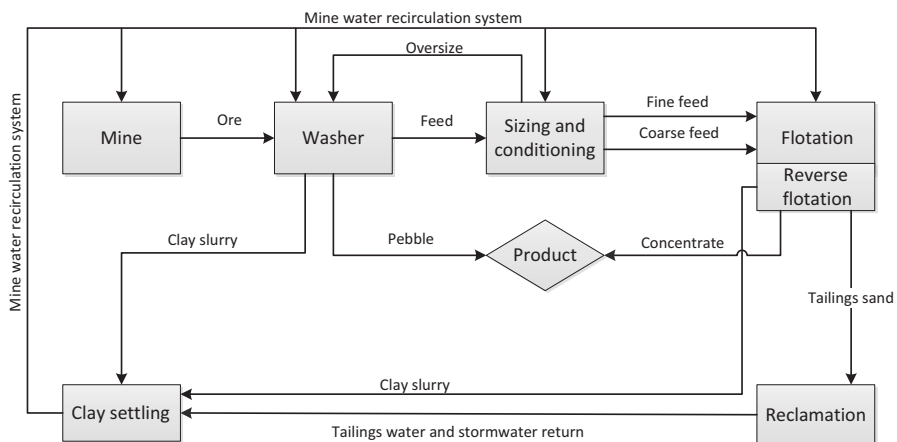


FIG. 10. Basic mining and beneficiation process used in Florida, USA.



FIG. 11. Phosphate rock (pebble).

further processing. The clay particles removed from the slurry during the washing process are usually pumped through pipelines to clay storage ponds where the clay slowly settles to the bottom. Clear water is drawn from the top of the pond and pumped back to the beneficiation plant for reuse.

Depending on the characteristics of the ore and the desired quality of the phosphate rock product, ore that has been wet screened may occasionally require no further processing other than dewatering (either naturally or using a centrifuge) and kiln drying. Usually, however, the ore needs to be further upgraded. It is sent to a flotation plant (see Fig. 12) in which various reagents such as fuel oil, soap and fatty acids are used to separate the phosphate particles from residual sand particles. These reagents coat the phosphate particles, allowing increased bonding with the air bubbles released from the bottom of the flotation chamber. The phosphate particles attached to the bubbles are transported to the top of the chamber where they are skimmed off mechanically, as shown in Fig. 13, and scrubbed with dilute sulphuric acid to remove the organic reagents. The material is then frothed with amines to float the remaining quartz. The phosphate rich fraction is pumped to large dewatering vessels, dried and stored in preparation for despatch as 'phosphate rock', the final product of the beneficiation process (see Fig. 14). The sand is pumped back into the mining void



FIG. 12. Flotation plant (courtesy: Florida Industrial and Phosphate Research Institute).



FIG. 13. Flotation column cell (courtesy: Florida Industrial and Phosphate Research Institute).



FIG. 14. Phosphate rock (concentrate).

(see Fig. 15) or stockpiled for future use, for example in land remediation. An aerial view of a typical beneficiation plant, illustrating the general plant layout, is shown in Fig. 16 and a closer view of the layout of the beneficiation process is shown in Fig. 17.

Depending on the mineralogy of the ore body, additional process steps may be included in the beneficiation process to remove specific impurities. For instance:

- (a) Some phosphate ores contain significant amounts of calcium carbonate (in the form of dolomite or calcite) and/or carbonaceous gangue and organic material. For such ores, a calcining step may be included in the beneficiation process.¹³ This involves heating the material to 800–950°C to decompose the impurities and facilitate their removal. The calcining process also improves the reactivity of the rock. Calcining is known to be used in India and Morocco and has been proposed for use in future operations in Saudi Arabia.



FIG. 15. Sand tailings pumped back to the mine cut (courtesy: Florida Industrial and Phosphate Research Institute).

¹³ Calcining is a process in which a material is heated to a high temperature without fusing, so that hydrates, carbonates or other compounds are decomposed and the volatile material expelled.



FIG. 16. Overall beneficiation plant layout.

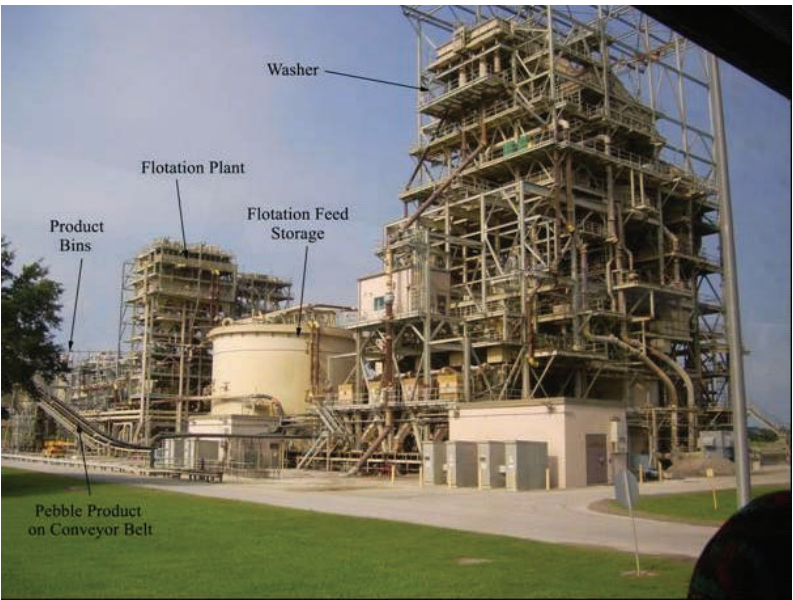


FIG. 17. Layout of the beneficiation process.

- (b) Some igneous ores contain significant amounts of iron, much of which may be removed by magnetic separation techniques. Such techniques are known to be used in Brazil, Canada, Egypt and South Africa.

Specific impurities removed from the ore are sometimes recovered as by-products. In South African igneous phosphate operations, for instance, copper sulphide concentrate and magnetite are recovered for smelting and for use in coal washing, respectively. In some Brazilian operations, baryte and/or magnetite are recovered as by-products.

Data on the chemical composition of phosphate rock are given in Appendix IV. The beneficiation process, by its very nature, gives the phosphate rock a more consistent composition than that of the original ore and, of course, a higher P_2O_5 content. The composition can be summarized as follows:

For phosphate rock of sedimentary origin, the P_2O_5 content is 23–37%. The other major component is CaO, with a concentration of 44–52%. The content of P_2O_5 and CaO combined (tricalcium phosphate) is 80–85%.

Phosphate rock of igneous origin contains higher concentrations of both P_2O_5 (35–42%) and CaO (51–54%). The content of P_2O_5 and CaO combined (tricalcium phosphate) is about 90%.

The fluorine content of phosphate rock (2–4%) is not appreciably different from that found in the ore.

The cadmium content of phosphate rock of sedimentary origin is highly variable within the range 0–100 ppm, whereas the cadmium content of phosphate rock of igneous origin is consistently low (0.25–2 ppm).

Maintenance of the beneficiation plant typically involves the removal of scale and the generation of surface contaminated scrap metal. As there are no chemical changes to the material during the beneficiation process, the selective precipitation of specific elements, including radioactive species, has not been found. Any scales observed consist of hardened phosphate rock or tailings material.

4.1.3. Bulk transport of phosphate rock

In highly industrialized phosphate producing countries such as the USA, it is common for the phosphate rock produced by the beneficiation process to be fed to a chemical processing plant located nearby, often on the same site. The transfer of the phosphate rock to the chemical process plant (or, in some cases, first to a milling facility) is accomplished either in dry form using rail cars, trucks or covered conveyors or as a slurry in a pipeline. When covered conveyors are used, workers using earth moving equipment push the rock from stockpiles into open chutes where the rock falls onto the conveyor.

In the less industrialized phosphate producing countries, it has been common practice for the phosphate rock to be exported without any further processing. This has necessitated the bulk transport of phosphate rock, often over very large distances, by sea, inland waterway, rail and/or road. However, this situation is changing as a result of increasing transport costs and the tendency for some major rock producing countries to focus more on 'value added' activities such as chemical processing and subsequent conversion into granulated fertilizer (see Section 2.5). As a result, the bulk shipment of rock is beginning to decline in favour of the shipment of fertilizer products.

4.2. RADIONUCLIDE ACTIVITY CONCENTRATIONS

4.2.1. Phosphate ore

Cationic radionuclide substitutions in the apatite structure of phosphate ore may include U^{4+} , U^{6+} , Th^{4+} , Ra^{2+} , Pb^{4+} , Pb^{2+} , Po^{4+} and Bi^{3+} . Substitutions may also occur in other minerals incorporated in phosphate ore or may be adsorbed on the surfaces of such minerals. The proportion of uranium substitutions involving the U^{4+} ion is reported to be 40–91% (mean 65%), with the balance involving the U^{6+} ion [42]. It is assumed that U^{4+} substitutes for Ca^{2+} in the apatite structure because these two ions have almost identical ionic radii. However, this type of substitution is limited because the number of Ca^{2+} ions is more than 25 000 times higher than the number of U^{4+} ions available for substitution and there are other, more plentiful, substitute ions available such as sodium and magnesium. Calcium ions may also be substituted with radium, lead, thorium and polonium ions. Uranium concentrations in phosphate ore are given in Table 7.

Data on radionuclide activity concentrations in phosphate ores are given in Appendix II. The following general conclusions can be drawn from these data:

- (a) In currently exploited sedimentary phosphate ores, the concentrations of individual ^{238}U series radionuclides generally range from about 0.5 to 3 Bq/g whereas the concentrations of ^{232}Th series radionuclides are generally not significantly elevated above values found in normal rocks and soils.
- (b) In currently exploited igneous phosphate ores, the concentrations of both the ^{238}U and the ^{232}Th series radionuclides are elevated (to about 0.1–0.2 Bq/g and 0.1–0.4 Bq/g, respectively). When compared with sedimentary phosphate deposits, the ^{238}U series radionuclide concentrations are lower but the ^{232}Th series radionuclide concentrations are higher.
- (c) In ores of both sedimentary and igneous origin, the ^{238}U and ^{232}Th decay chains are generally in radioactive equilibrium.

TABLE 7. URANIUM IN PHOSPHATE ORE (BY COUNTRY)

Country	Concentration of uranium as U_3O_8 (%)	Reference
Algeria	0.011–0.014	[12]
Brazil	0.008	[12]
India:		[30]
Mussorie	0.04	
Karnataka	0.03–0.08	
Israel	0.005–0.015	[12]
Jordan	0.012–0.015	[12]
	0.024	[43]
Morocco	0.009–0.014	[12]
	0.023	[44]
Tunisia	0.005–0.01	[12]
USA:		
Florida	0.015–0.018	[45]
North Carolina	0.008	[12]

Overall, the activity concentrations in currently exploited phosphate ores are about 0.1–3 Bq/g for radionuclides in the ^{238}U decay series and 0.1–0.4 Bq/g for radionuclides in the ^{232}Th decay series.

4.2.2. Phosphate rock

Data on the radionuclide activity concentrations in phosphate rock product are given in Appendix IV. In summary:

- (a) The ^{238}U concentrations in phosphate rock originating from sedimentary deposits generally fall within the range 0.2–2.5 Bq/g.

- (b) The ^{238}U concentrations are significantly lower in phosphate rock originating from igneous deposits (0.03–0.18 Bq/g).
- (c) The ^{232}Th concentrations in products of sedimentary origin, as well as in igneous product from Kola, Russian Federation, generally fall within the range 0.01–0.1 Bq/g.
- (d) The ^{232}Th concentrations in the igneous product from South Africa (0.3–0.4 Bq/g) are significantly higher than the levels found in most sedimentary products.
- (e) The situation regarding other radionuclides in the ^{238}U and ^{232}Th decay series is similar to that for the original phosphate ore. In most cases, the ^{238}U and ^{232}Th decay chains appear to be in approximate radioactive equilibrium [46, 47].

4.2.3. Tailings

A summary of available information on radionuclide activity concentrations in tailings is given in Table 8. The concentrations are generally similar to those in the ore from which they are derived, although for central Florida operations, this is true only for clay tailings — the radionuclide concentrations in sand tailings are typically an order of magnitude lower.

4.3. OCCUPATIONAL EXPOSURE

4.3.1. Exposure pathways

External exposure to gamma radiation occurs through proximity to bulk quantities of process materials, but the degree of such exposure is limited by several factors. Workers in the mining areas operate heavy equipment such as draglines and pit cars and this equipment provides a significant amount of shielding of the operators from gamma radiation. Workers in beneficiation plants spend only limited periods close to bulk material and are shielded by containers and liquids.

Internal exposure occurs through the inhalation of radionuclides in airborne dust while working in the operational areas of the mine and beneficiation plant. The excavation, conveying, crushing, grinding and other handling of dry phosphate rock can generate significant amounts of airborne dust. In the case of wet mining and beneficiation processes, however, dust inhalation is not a significant exposure pathway, even with the highest activity concentrations in known ore bodies, because dust is suppressed by the water used to break up and transport the ore. Exposure to airborne dust may also occur while handling waste

TABLE 8. RADIOACTIVITY IN TAILINGS FROM THE BENEFICIATION OF PHOSPHATE ROCK

Source	Activity concentration (Bq/g) ^a				
	U-238	Th-230	Ra-226	Th-232	Th-228
<i>Tailings from sedimentary ore^b</i>					
USA, central Florida (clay) [16, 47]	0.6–1.8	2.3	0.5–1.9	0.04	—
USA, central Florida (sand) [16, 47]	0.055–0.4	0.25	0.06–0.45	0.004	—
USA, northern Florida [47]	0.01–0.03	—	0.07–0.1	—	—
<i>Tailings from igneous ore</i>					
South Africa [48]	0.26 (0.22–0.30)	—	0.25 (0.19–0.28)	0.33 (0.26–0.44)	0.34 (0.22–0.46)

^a Some values have been rounded.

^b Higher values than those listed in the table have been encountered, but these are not representative of current commercial operations. In tailings from former sedimentary phosphate mining in the United Republic of Tanzania, the activity concentrations were 4.3 Bq/g for ²²⁶Ra and 0.6 Bq/g for ²²⁸Ra and ²²⁸Th [49].

materials and surface contaminated objects and while cleaning or refurbishing contaminated equipment.

In opencast mining operations, no significant buildup of radon daughters occurs. Similarly, beneficiation plants are open to outside air exchange and there is again little opportunity for the buildup of radon progeny above ambient levels. If mining is conducted underground, opportunities exist for the significant buildup of radon progeny in the workplace atmosphere, with the extent of any such buildup depending strongly on the ventilation conditions.

4.3.2. Exposure levels

4.3.2.1. Gamma dose rates

For the relatively low concentrations of ²³⁸U and ²³²Th decay series radionuclides in phosphate ore and phosphate rock, the dose rate depends primarily on the activity concentration of the material rather than its total quantity and geometry. Using a theoretical modelling technique described in Ref. [50], gamma dose rates per unit activity concentration have been calculated at a

distance of 1 m from a 1000 m³ volume of material in which radionuclides in each of the ²³⁸U and ²³²Th decay series were assumed to be in equilibrium. The predicted dose rate associated with uranium series radionuclides is 0.39 µSv/h per unit activity concentration of ²³⁸U (in becquerels per gram). For thorium series radionuclides, the corresponding figure is 0.58 µSv/h per unit activity concentration of ²³²Th. The predicted dose rate from ⁴⁰K is 0.04 µSv/h per Bq/g. These dose factors have been applied to phosphate ore and phosphate rock using radionuclide activity concentrations selected from Appendix II and Appendix IV, respectively.¹⁴ The results are given in Table 9. In Ref. [51] a mean dose rate of 0.54 µSv/h was calculated for 14 worldwide rock sources. Excluding an unrepresentative value for Tanzanian rock, the mean dose rate was 0.39 µSv/h. These values are consistent with those given in Table 9.

Gamma dose rates measured at two mines and beneficiation plants in the Syrian Arab Republic [52] are shown in Table 10. These results are very similar to the theoretical values reported in Table 9.

Extensive area monitoring using thermoluminescent dosimeters (TLDs) in rock tunnels used for transporting rock to a phosphoric acid plant in central Florida, USA, was carried out over a period of four years. The absorbed dose rates were in the range 0.08–3.4 µGy/h and rarely exceeded 1 µGy/h. The average absorbed dose rate was 0.18 µGy/h [53].

Gamma dose rates from phosphate ore can be summarized as follows:

- (a) Dose rates associated with sedimentary material are generally a few tenths of a microsievert per hour, rarely exceeding 1 µSv/h, with the ²³⁸U series radionuclides contributing almost the entire dose.
- (b) Dose rates associated with igneous material are 0.1–0.3 µSv/h, significantly lower than those associated with sedimentary material. Material from Kola, Russian Federation, gives significantly lower dose rates than material from South Africa. About 60–80% of the dose is attributable to the ²³²Th series radionuclides, with the ²³⁸U series radionuclides contributing most of the balance.

¹⁴ In order to demonstrate the relative contribution of all radionuclides, only data sets that included activity concentrations of ²³⁸U and ²³²Th series radionuclides as well as ⁴⁰K were selected from Appendices II and IV. Some ⁴⁰K concentrations were determined from the K₂O content given in Appendix IV.

TABLE 9. GAMMA DOSE RATES NEAR LARGE VOLUMES OF PHOSPHATE ORE AND PHOSPHATE ROCK, PREDICTED FROM RADIONUCLIDE ACTIVITY CONCENTRATIONS

Source	Activity concentration (Bq/g)			Dose rate			
	U-238	Th-232	K-40	Total (μSv/h)	Contribution to total		
					U-238	Th-232	K-40
<i>Material of sedimentary origin</i>							
Phosphate ore:							
Sudan (Uro)	4.0 (Ra-226)	0.01	0.06	1.6	>99%	<1%	<1%
Sudan (Kurun)	0.4 (Ra-226)	0.01	0.14	0.2	95%	2%	3%
USA (central Florida)	0.8–3.1	0.02	0.003–0.019	0.3–1.2	98%	2%	<1%
Egypt	0.4	0.02	0.05	0.2	91%	8%	<1%
Phosphate rock:							
Morocco	0.9–1.9	0.01–0.03	0.03 ^a	0.4–0.8	98%	2%	<1%
Togo	1.0–1.5	0.03–0.1	0.01–0.03 ^a	0.4–0.6	93%	7%	<1%
USA (central Florida) (pebble)	1.3–2.5	0.03	0.03 ^a	0.5–1.0	97%	3%	<1%
USA (central Florida) (concentrate)	0.7–1.8	0.02	0.03 ^a	0.3–0.7	97%	3%	<1%
Egypt	0.4–0.5	0.02–0.04	0.02	0.2	92%	7%	<1%
Algeria	0.6	0.06	0.02	0.3	87%	12%	<1%
Jordan	0.8–1.0	0.002–0.02	0.01–0.15	0.3–0.4	98%	1%	<1–2%
Tanzania (Arusha)	4.1–4.6	0.61–0.63	0.29	2.0–2.2	83%	17%	<1%
Tunisia	0.8	0.03	0.03	0.3	95%	5%	<1%
<i>Material of igneous origin</i>							
Phosphate ore:							
Russian Federation (Kola)	0.07	0.1	0.1	0.1	31%	65%	4%
South Africa	0.2	0.4	0.003–0.02 ^a	0.3	25%	75%	<1%

TABLE 9. GAMMA DOSE RATES NEAR LARGE VOLUMES OF PHOSPHATE ORE AND PHOSPHATE ROCK, PREDICTED FROM RADIONUCLIDE ACTIVITY CONCENTRATIONS (cont.)

Source	Activity concentration (Bq/g)			Dose rate			
	U-238	Th-232	K-40	Total (μSv/h)	Contribution to total		
					U-238	Th-232	K-40
Phosphate rock:							
Russian Federation (Kola)	0.03–0.1	0.06–0.09	0.14	0.1	31%	60%	8%
South Africa	0.1–0.2	0.3–0.6	0.003–0.02 ^a	0.2–0.4	18%	82%	<1%

^a Estimated from the potassium content of the phosphate rock (see Table 51, Appendix IV).

TABLE 10. GAMMA DOSE RATES MEASURED AT TWO MINING AND BENEFICIATION FACILITIES IN THE SYRIAN ARAB REPUBLIC

Personnel	Al-Sharkeia mine		Khnefees mine	
	Occupancy (%)	Dose rate (μ Sv/h)	Occupancy (%)	Dose rate (μ Sv/h)
Mine workers	37	0.4	37	0.5
	3	0.3	3	0.3
	4	0.2	4	0.1
Plant workers	30	0.2	30	0.1
	15	0.3	10	0.3
			5	0.5
Administrative workers	46	0.1	41	0.1
Maintenance workers in workshops	30	0.1	30	0.1

4.3.2.2. *Inhalation of airborne dust*

Measurements of airborne dust activity concentrations in sedimentary phosphate mining and beneficiation facilities in Florida, USA, are reported in Ref. [53]. Dust samples were collected on filters using either a high volume stationary air sampler or low volume personal air samplers. Alpha counting of the dust samples suggested an airborne ^{238}U activity concentration of 5–10 mBq/m³ in the mining area. Higher dust levels, up to 100 mBq/m³, were measured in the crushing, grinding and screening areas of the beneficiation plant. Although some of the dust levels were high, the occupancy periods of workers were reported to be only a small fraction of the total working period. In addition, workers were often required to use respiratory protective equipment as part of normal OHS procedures.

4.3.2.3. *Inhalation of radon*

Radon exposures were measured at two mining and beneficiation facilities in the Syrian Arab Republic [52], at mining and beneficiation plants in central Florida, USA [53], and in underground mines in Egypt [54, 55]. The results are summarized in Table 11. Assuming an equilibrium factor of 0.4 and an annual working period of 2000 h, the potential alpha energy exposures at Syrian facilities (0.3–1.1 mJ·h·m⁻³) imply an annual average radon concentration of about 65–245 Bq/m³. Elevated exposures of administrative workers at the Al-Sharkeia mine were reportedly caused by the offices being built on phosphate sands and being poorly ventilated, especially in winter. Remedial action in these particular workplaces was proposed. At beneficiation plants in Florida, USA, the radon concentrations in the flotation plant, pit cars and railcar loading area were consistent with indoor radon concentrations. Measurements were also made in mining and rock handling areas. With the exception of rock tunnels, background levels were not exceeded. The high radon and radon progeny concentrations measured in Egyptian underground mines were the result of poor ventilation.

4.3.3. **Effective dose**

4.3.3.1. *Gamma radiation*

Annual effective doses received by workers from external gamma radiation have been assessed using data from three countries and are summarized in Table 12. In the Syrian Arab Republic, doses received by workers in two sedimentary phosphate mining and beneficiation facilities have been determined from the dose rate

TABLE 11. EXPOSURES TO RADON AND RADON PROGENY MEASURED AT PHOSPHATE MINING AND BENEFICIATION FACILITIES

Facility and location	Rn-222 EEC ^a (Bq/m ³)	Rn-222 activity concentration (Bq/m ³)	Mean annual potential alpha energy exposure (mJ·h·m ⁻³)
Syrian Arab Republic (Al-Sharkeia and Khnefees mines) [52]:			
Mines			0.4
Plants			0.5–1.1
Maintenance workshops			0.3
Administrative offices			0.4–1.1
Central Florida, USA [53]:			
Flotation plant, pit cars, railcar loading area		18.5–59.3	
Rock tunnels		214–1481	0.02–0.46
Egypt [54, 55]:			
Abu-Tartar mine	1800–5500		9
Safaga, Hamraween and ElQuser mines	1250–2700		

^a Radon EEC (equilibrium equivalent concentration) is the activity concentration of radon in radioactive equilibrium with radon progeny that would have the same potential alpha energy concentration as the actual (non-equilibrium) mixture.

measurements reported in Table 10 [52]. In South Africa, doses received by workers in an igneous phosphate mining and beneficiation facility have been determined from measurements made with a portable gamma dose rate meter [56, 57]. In central Florida, USA, doses received by workers in sedimentary phosphate facilities have been determined from external exposure measurements using both lithium fluoride thermoluminescence dosimeters (LiF TLDs) and the more sensitive aluminium oxide carbon-doped luminescence dosimeters (Al₂O₃:C OSLDs) [53].

4.3.3.2. *Inhalation of airborne dust*

Annual effective doses received by workers from the inhalation of airborne dust are reported from facilities in South Africa and the USA and are summarized in Table 12. The doses were assessed from measurements conducted with personal air samplers (South Africa) or high volume stationary air samplers (USA).

TABLE 12. DOSES RECEIVED BY WORKERS IN PHOSPHATE MINING AND BENEFICIATION FACILITIES

Worker location	Mean annual effective dose (mSv)		
	Gamma radiation	Inhalation of airborne dust	Total
Syrian Arab Republic (sedimentary phosphate) [52]: ^a			
Mine workers	1.3 ^b ; 1.6 ^c		
Plant workers	0.8		
Administrative workers	0.4		
Maintenance workers in workshops	0.3		
South Africa (igneous phosphate) [56, 57]:			
Mining:			
Operational areas	0.42	0.70	1.12
Crushers	0.35	0.77	1.13
Workshops	0.09	0.58	0.66
Mine mobile equipment	0.66	0.51	1.17
Milling:			
Operational areas	0.10	0.19	0.29
Workshops	0.00	0.09	0.09
Beneficiation:			
Magnetic separation	0.05	0.19	0.24
Flotation operational area	0.23	0.09	0.32
Flotation workshop	0.67	0.09	0.76
Filtration operational area	0.05	0.27	0.32
Filtration workshop	0.00	0.09	0.09
Drying and storage	0.80	0.17	0.97
Dispatch	0.20	0.16	0.36
USA (sedimentary phosphate) [53]	0.168 ^d ; 0.095–0.114 ^e	0.005–0.060	0.12–0.30 ^e

^a Doses from inhalation of airborne dust were not determined.

^b Al-Sharkeia mine.

^c Khnefees mine.

^d Determined from LiF TLD measurements.

^e Determined from Al₂O₃:C OSLD measurements.

4.3.3.3. *Total effective dose*

For an igneous phosphate mining and beneficiation facility in South Africa, summing of the doses from external gamma exposure and inhalation of airborne dust gives total annual effective doses in the range 0.1–1 mSv (Table 12). The mean total annual effective dose received by workers in sedimentary phosphate mining and beneficiation facilities in Florida, USA, was calculated from measured exposure levels and found to be in the range 0.12–0.30 mSv [53]. In the mining area at this plant, 75% of the total dose arises from external exposure whereas in ore crushing, grinding and screening locations the reverse is the case, with the majority of the dose arising from internal exposure.

4.3.4. **Transport of material**

External gamma dose rates and annual doses received by workers involved in the transport of phosphate rock are reported in Refs [58, 59]. Doses received from external exposure to gamma radiation were calculated from exposure measurements and estimated maximum exposure periods. The results are shown in Table 13. With respect to sea transport, gamma dose rates arising from the loading of sedimentary phosphate rock originating from Morocco and Florida, USA, were found to be elevated above background levels, whereas the corresponding dose rates for igneous rock from Kola, Russian Federation (not shown), were not elevated. Dose rates for inland transport by ship were measured on a barge loaded with phosphate rock originating from Morocco and having activity concentrations at the upper end of the normal range. As expected, the highest doses were those arising from loading operations, owing to the closer proximity of the workers involved. Exposures during rail transport occur only while loading and unloading. Exposures for truck transport occur during loading and unloading and during transport as measured in the truck cab. The annual doses received by workers were all significantly less than 1 mSv.

4.4. PUBLIC EXPOSURE

Members of the public in the vicinity of phosphate rock mining and beneficiation operations may be exposed through the following pathways:

- (a) Inhalation of dust and radon dispersed from the operations;
- (b) Ingestion of groundwater contaminated with radionuclides migrating from the mining and tailings management facilities;

TABLE 13. EXPOSURE OF WORKERS INVOLVED IN THE TRANSPORT OF PHOSPHATE ROCK [58]

Exposure situation	Dose rate (μSv/h)	Annual dose (mSv)
Sea transport, loading	0.10	0.09
<i>Inland ship:</i>		
Loading	0.26	
Transport	0.10	
Overall		0.18
Railway, loading and unloading	0.26	0.29
<i>Truck:</i>		
Loading and unloading	0.26	
Transport	0.16	
Overall		0.33

- (c) Ingestion of foodstuffs affected by water and soil contamination through leaching and dust fallout;
- (d) External gamma radiation from contaminated soil and bulk residues.

Exposure of members of the public, irrespective of the pathway involved, is likely to be very low because mining and beneficiation operations tend to be conducted at considerable distances from residential areas and involve materials with low activity concentrations. Most rock handling and processing operations are conducted under wet conditions. Under unfavourable wind conditions, it is possible for members of the public to be exposed to radionuclides in airborne dust generated by the crushing, milling and drying of rock. The migration of radionuclides from mining and residue management facilities into water bodies could result in the contamination of drinking water and food but, again, this exposure pathway is not expected to be significant, particularly because process water is usually recycled within the facility.

A study was conducted to determine if there was an elevated health risk due to ingestion of radionuclides (²²⁶Ra and ²¹⁰Pb) or toxic metals (cadmium, lead and mercury) in fish harvested from lakes on previously mined lands in the central Florida phosphate region [60]. The study examined ten lakes in total:

- (a) Four unreclaimed lakes (pit lakes that are formed when strip mining cuts fill with water and the site is abandoned for nature to recover with no attempt to reclaim the land);

TABLE 14. ESTIMATED INCREMENTAL DOSE RECEIVED BY A MEMBER OF THE PUBLIC LIVING NEXT TO AN IGNEOUS PHOSPHATE MINING AND BENEFICIATION FACILITY [61]

Source of dose	Annual committed effective dose (rounded) (μSv)
Gamma radiation from soil	0.004
<i>Inhalation:</i>	
Airborne dust	16
Radon	1
<i>Ingestion:</i>	
Leafy vegetables	0.1
Root vegetables	0.3
Fruit	0.1
Meat	3
Milk	0.6
Cereals	0.1
Poultry	0.2
Eggs	0.07
Total	21

- (b) Two reclaimed lakes (lakes created as part of the mining process that are contoured, vegetated and stocked with fish to resemble and function like natural lakes);
- (c) Three natural lakes (lakes in the study area that were formed by natural means and regarded as ‘control’ lakes unaffected by mining);
- (d) One reservoir (an artificially constructed lake that was unrelated to phosphate mining).

Six species of fish were sampled, representing those most commonly consumed by humans. The radionuclide data indicated no significant health risk attributable to the former mining activities. Radium is known to concentrate in bones, but the bones of fish are not normally consumed in the study region and so the risk from bones was largely discounted. There was no difference in lead or cadmium levels among the different types of lake. However, it was noted that mercury levels in fish from natural lakes were higher than in those from the mining-impacted lakes and may be due to the fact that natural lakes tend to be

much older and have greater surface to volume ratios (more shallow areas), which provide more time and surface area to capture global fallout of mercury.

Another study in Florida, USA, surveyed radioactivity in food produced from a variety of land types, including mined lands (concentrating on lands which were reclaimed after phosphate mining) and unmined lands underlain with phosphate deposits [62]. More than 100 food samples were collected from 62 land parcels and analysed. This was followed by a study that investigated, more broadly, the presence of radioactivity in locally grown or caught foods, concentrating mainly on foods grown on reclaimed clay lands [63]. In extensive studies of foods grown on mined lands [62, 63], the doses were found to be trivial (less than 10 $\mu\text{Sv/a}$).

Approximately 70 individual food samples were collected from five land parcels in the central Florida phosphate district and analysed for ^{226}Ra , ^{210}Pb and ^{210}Po . Corresponding soil samples were collected and analysed both for these radionuclides and for a variety of soil chemistry parameters. The results of the radioactivity and soil chemistry analyses of these samples were integrated into the database, which had been created from the initial study, and a variety of statistical analyses were conducted on this integrated data set [63]. The results of these analyses indicated that the concentrations of ^{226}Ra and ^{210}Pb in edible crops grown on mined phosphate lands were statistically higher than those in crops grown on unmined phosphate lands. However, the ^{210}Po concentrations were extremely low, with many being below the lower limit of detection, and the dose from food consumption was only a small fraction of that received by an average individual from other environmental sources of radioactivity. An individual who sourced all the sampled food types from the reclaimed clay land areas and all remaining food types from the general food pool was estimated to receive a committed effective dose of 191 μSv in a year from food consumption. By comparison, the corresponding ingestion dose received by an individual obtaining all food from the general food pool was estimated to be 164 μSv . Thus, the incremental ingestion dose attributable to the former mining operation was only 27 μSv per year. Two beef samples were analysed, one from mined land and one from unmined land. Each sample was replicated three times, yielding a total of six beef observations. The geometric mean values of ^{226}Ra activity concentration were 0.000147 and 0.000126 Bq/g for mined and unmined land, respectively. The difference between these results is statistically insignificant.

A dose assessment was conducted at an igneous phosphate mining and beneficiation facility in South Africa [61]. The assessment considered a member of the public residing on the perimeter of the facility, with all drinking water being obtained from an external source that was not influenced by the operation of the facility. The doses attributable to the operation of the facility were estimated from measurements of the concentrations of radionuclides in various

environmental media, including surface water, groundwater and food, using conservative assumptions. The results are given in Table 14.

4.5. REGULATORY CONSIDERATIONS

In terms of the Standards, it is unnecessary to regulate (as a practice) material in which the activity concentrations of radionuclides in the uranium and thorium decay chains do not exceed 1 Bq/g. This criterion is of particular relevance to the mining and beneficiation of phosphate ore because the radionuclide activity concentrations in the materials involved are all rather moderate and may well be less than 1 Bq/g. Moreover, the nature of the processes involved is such that radionuclides do not become concentrated in scale and other deposits inside pipes and vessels, so the application of the 1 Bq/g criterion would generally require only a knowledge of the activity concentrations in the ore, phosphate rock and tailings.

4.5.1. Mining and beneficiation of phosphate ore of igneous origin

All radionuclide activity concentrations in the phosphate ore, phosphate rock and tailings are less than 1 Bq/g, implying that it is not necessary to regulate the mining and beneficiation of ore of igneous origin. This conclusion is supported by dose assessments which show that the annual effective doses received by workers and by members of the public do not exceed 1 mSv by any significant amount. The adoption of good OHS and environmental protection practices (not specifically aimed at radiological concerns) are likely to bring about further reductions in the already low levels of radiation exposure.

4.5.2. Mining and beneficiation of phosphate ore of sedimentary origin

While the activity concentrations of radionuclides in the ^{232}Th decay series in the phosphate ore, phosphate rock and tailings are all less than 1 Bq/g, the same is not always true of the radionuclides in the ^{238}U decay series. For those operations in which the activity concentrations of radionuclides in the ^{238}U decay series exceed 1 Bq/g, the doses received by workers and by members of the public need to be taken into account when considering the possible need for regulation as a practice. All indications are that in such situations, the doses arising from external gamma exposure and inhalation of airborne dust are unlikely to exceed 1 mSv. In those few instances where the ore is mined by underground methods, the radon concentrations to which the underground workers are exposed would have to be considered.

It can be concluded that most mining and beneficiation operations involving material of sedimentary origin are candidates for exemption by the regulatory body, particularly if the operation is known to be conducted in accordance with good OHS and environmental protection practices. For some operations, a requirement for notification and even authorization in the form of a registration might be appropriate if there are concerns about airborne dust and contamination of water bodies. It may be necessary for the regulatory body to ensure that measures are in place to:

- (a) Minimize airborne dust both inside and outside the plant;
- (b) Control the way in which process water is managed; and/or
- (c) Monitor the quality of nearby groundwater and surface water bodies.

In the case of underground mining, remedial action to reduce radon concentrations through improved ventilation might also be needed.

4.5.3. Transport of bulk material

The radionuclide activity concentrations of phosphate ore, phosphate rock and tailings are well below the levels at which the Transport Regulations would become applicable (see Section 3.1.3). Consequently, such material can be transported without any restrictions or controls of a radiological nature. This conclusion is supported by the results of dose assessments carried out for various transport scenarios.

5. PRODUCTION OF PHOSPHORIC ACID BY THE WET PROCESS

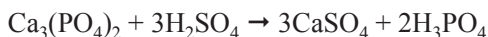
5.1. PROCESS DESCRIPTION

Digestion of phosphate rock with sulphuric acid is by far the most common type of wet process used for phosphoric acid production. Digestion with hydrochloric acid is used to a lesser extent for producing high purity phosphoric acid for use in foodstuff applications.

5.1.1. Sulphuric acid digestion

5.1.1.1. Main process

A mixture of sulphuric acid and recycled phosphoric acid is added continuously to phosphate rock in a reactor vessel or ‘attack tank’. The rock is digested by the sulphuric acid to produce phosphoric acid and calcium sulphate, known as phosphogypsum. Each tonne of P_2O_5 produced in the form of phosphoric acid is matched by 4–6 t of phosphogypsum (dry weight). The basic chemical reaction can be represented by:



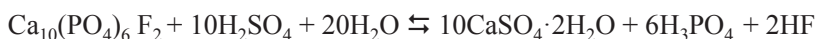
As the rock particles react, they tend to become coated with an insoluble layer of calcium sulphate, hindering further reaction. The presence of the recirculated phosphoric acid, as well as control over the rock particle size, minimizes this problem. The sequential chemical reactions are as follows:



and



The chemical reaction for the digestion of fluorapatite may be expressed as follows:



Following acid attack, the resulting phosphoric acid is transferred to one or more filtration assemblies, commonly of the tilting pan type (see Fig. 18), in order to separate the acid from the phosphogypsum.¹⁵ The phosphogypsum is in a hydrated form, the degree of hydration depending on the process conditions, in particular the temperature, the P_2O_5 concentration and the free sulphate content. The main forms of phosphogypsum produced are the dihydrate form ($CaSO_4 \cdot 2H_2O$) and the hemihydrate form ($CaSO_4 \cdot \frac{1}{2}H_2O$). After separation from

¹⁵ Less commonly, either rotary table or travelling belt filtration is used.



FIG. 18. Tilting pan filtration equipment.

the phosphoric acid, the wet phosphogypsum is sent to a residue pile (stack) for storage, usually after washing to remove traces of phosphoric acid and fluoride. The default condition for the subsequent use of phosphogypsum is the dihydrate form, since the hemihydrate and other hydrate forms convert rapidly to the dihydrate form. The rehydration process may begin even before separation from the phosphoric acid and the conditions for rehydration become more favourable still during washing and upon exposure to environmental moisture during transport and storage.

Several variants of the sulphuric acid digestion process are in commercial use [64] and are summarized in Appendix V. Each method has its advantages and disadvantages, with the choice of method in a particular situation depending on a variety of considerations, such as the complexity and cost of the processes and process equipment involved, the nature and level of experience of plant personnel, limitations on the quality and particle size of the feedstock material, the efficiency of P_2O_5 recovery and the quality of the phosphoric acid and phosphogypsum produced [65]. Most of the early phosphoric acid plants used one of the simpler methods based on dihydrate phosphogypsum production. The desire for improvements in energy efficiency, P_2O_5 recovery and phosphoric acid purity has led to a growth in popularity of methods based on hemihydrate

phosphogypsum production, although these improvements have come at the cost of greater challenges for plant operators.

The compositions of the process materials are not easy to characterize in terms of origin or country since each manufacturing facility has its own strategy for obtaining phosphate rock feedstock, often depending on availability and economic factors. Heavy metals (such as arsenic, cadmium, chromium, lead and mercury) and fluoride originating from the ore become distributed between the phosphoric acid and phosphogypsum products, the exact distribution being very much dependent on the type of phosphate ore, the process and the type of impurity.

The phosphoric acid reactor is drained and cleaned periodically, typically annually. The thickness of the scale that accumulates on the walls of the reactor ranges from several centimetres to a metre or more. Scale may also accumulate on the roof of the tank, particularly near the point where the sulphuric acid is added. The scale consists predominantly of phosphogypsum and non-radioactive compounds such as sodium fluosilicate (Na_2SiF_6) and sodium potassium fluosilicate (NaKSiF_6). Removal of the scale is accomplished by high pressure water jetting and mechanical equipment.

The acid leaving the reactor contains residual minerals that are dissolved at saturation or supersaturation levels. These minerals are subsequently precipitated, leading to the accumulation of sediment and the deposition of radium rich scale on the relatively cool internal surfaces of pipes, vessels and filtration equipment. If allowed to build up, this sediment and scale can seriously reduce the flow capacity of pipes and interfere with the functioning of the filtration equipment. To help prevent this, the lines in a phosphoric acid plant are flushed every 1–2 weeks to purge the solids that have settled out and remove some of the scale adhering to the pipe walls. In addition, the filtration pans are periodically cleaned by dry chipping and abrasion and the filtration cloths that cover the tilting pans are replaced (see Fig. 19). Since flushing does not remove all the scale, some pipes affected by scaling are eventually replaced.

The buildup of residues such as scale in pipes and filtration equipment can be minimized by refinements to the production process [66]. As an example, in plants using the hemihydrate method (see Appendix V), scale formation can be eliminated by the incorporation of a simple hemihydrate rehydration step or by the addition of a small quantity of anti-scaling agent to the single stage filtration system.



FIG. 19. Maintenance worker replacing the filter cloth on a tilting pan filtration assembly (courtesy: Florida Industrial and Phosphate Research Institute).

5.1.1.2. Further processing of phosphoric acid

Phosphoric acid emerging from the filtration step in any of the ‘weak acid’ methods (see Appendix V) has a P_2O_5 content in the range 24–36% and a typical residual solids content of some 2%. For most industrial applications, additional concentration and/or purification steps are required. First, the strength of the phosphoric acid is increased by evaporation to 40–55% P_2O_5 . The design of the evaporation equipment takes account of the corrosive nature of the phosphoric acid and the very high scaling characteristics of the vapour released during the concentration process. The heat exchangers are fabricated from graphite or stainless steel, while the remaining equipment is made from rubber lined steel. An example of the acid composition at this stage, prior to further purification, is given in Table 15.

In many plants, a flocculant is then added to the acid and the solids are settled in a clarifier. At about 40% P_2O_5 , the solubilities of residual fluosilicates and phosphogypsum are both at a minimum. As a result, many plants use this property to clarify the acid at the 40% level. The clarifier underflow contains, in

TABLE 15. EXAMPLE OF PHOSPHORIC ACID COMPOSITION PRIOR TO PURIFICATION [48]

Main chemical constituents (%)		Trace elements (ppm)	
P ₂ O ₅	55	Cl	175
MgO	2	As	14
Al ₂ O ₃	0.05	Cd	2
Fe ₂ O ₃	0.45	Cu	200
K ₂ O	0.04	Pb	1
Na ₂ O	0.05	V	20
SO ₄ ²⁻	3.18	Mn	250
F ⁻	0.28	Sr	2
		Cr	30

addition to fluosilicates and phosphogypsum, minor amounts of magnesium, aluminium and fluorine compounds and is sent back to the attack tank or to a separate filter for recovery of the remaining phosphate. Scale builds up on the walls of the 40% clarifiers and surge tanks. Since the buildup is slow, it does not require periodic removal. When the tanks eventually need to be relined, the scale is fully removed using a combination of high pressure water jetting and mechanical equipment.

Other purification methods such as solvent extraction, crystallization and ion exchange may also be used to remove impurities from the phosphoric acid. In the solvent extraction purification process, the H₃PO₄ is extracted by passing the crude acid through one or more organic phase extraction columns using a solvent such as a short chain (4–8 carbon atoms) alcohol, ketone, ether or amine. This technique removes 60–75% of the P₂O₅ contained as an impurity in the crude acid and converts it to H₃PO₄. The purified acid is then recovered in the backwash step using countercurrent extraction and concentrated to achieve the required P₂O₅ content.

Further concentration of phosphoric acid beyond 40–55% P₂O₅ causes various phosphates to precipitate. A typical formulation is (Fe)₃NaH₁₄(PO₄)₈, where aluminium can substitute for iron and ammonia and potassium can substitute for sodium, depending on availability [67]. These solids, which contain more than 50% P₂O₅, may be left suspended in the acid or may be removed by settling in a clarifier or by centrifuging, the choice being dictated by the final product specifications.

The P_2O_5 content of phosphoric acid may be further increased by partially converting it from the orthophosphoric form (H_3PO_4) to polyphosphate forms, resulting in a product known as superphosphoric acid. The process involves a condensation reaction in which two or three orthophosphoric acid molecules are converted into higher polymeric forms. The basic chemical reactions are:



and



The P_2O_5 content of superphosphoric acid is very high, exceeding even that of 100% orthophosphoric acid. Such high P_2O_5 concentrations are achieved by evaporating essentially all of the free moisture, including that generated in the condensation of the orthophosphate, using high pressure evaporation units. The colour of superphosphoric acid is either light green ('green superphosphoric acid') or black ('black superphosphoric acid'), depending on whether the orthophosphoric acid from which it is derived has been manufactured from calcined rock or uncalcined rock, respectively. Most green superphosphoric acid is used for the manufacture of 10-34-0 liquid ammonium polyphosphate fertilizer, a product containing 60% $(NH_4)_3PO_4$ and 40% H_2O . The high polymeric content allows the sequestration of other cationic metals, such as iron, aluminium, magnesium and zinc. The product is often used to carry these micronutrients to the recipient crops. Black superphosphoric acid may either be sold as such for industrial uses or further processed by oxidation to produce green superphosphoric acid.

The production of superphosphoric acid typically begins with acid having a strength of 40–47% P_2O_5 that has been clarified to remove some of the magnesium, aluminium and fluorine compounds that precipitate out at that strength. After concentrating to a strength of 54% P_2O_5 , the acid is fed into an alloy evaporator. Further concentration leads to the conversion of about 25–30% of the P_2O_5 content from the orthophosphate form to polyphosphate forms, giving a final product strength of at least 70% P_2O_5 . In a variation of this process, several manufacturers in the USA use feed acid that has been subjected to minimal clarification and remove the impurities later in the process by subjecting the superphosphoric acid to pressure filtration. Scale formation occurs during the production of superphosphoric acid [68].

Figure 20 shows the scale inside a pipe in a green superphosphoric acid plant that was found to contain fluorine rich compounds, while Fig. 21 shows the

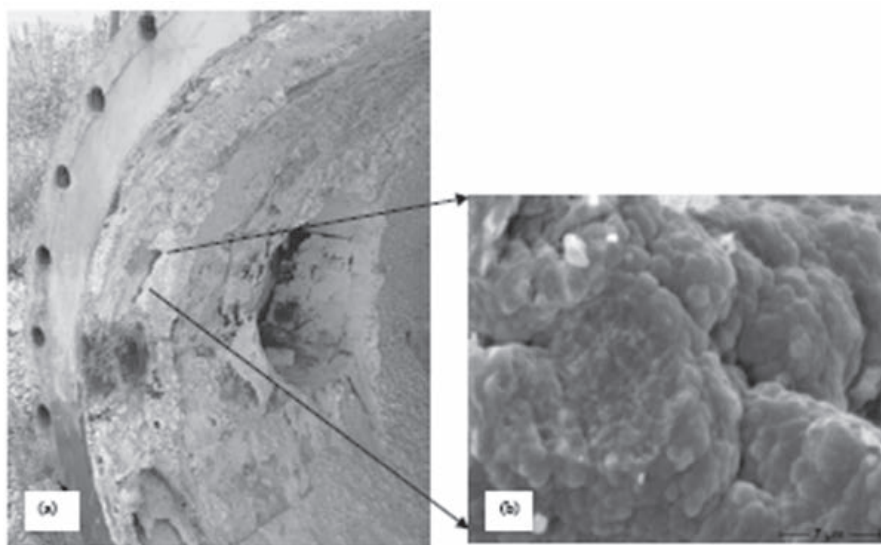


FIG. 20. Pipe scale observed in a green superphosphoric acid plant [68].

scale inside a green superphosphoric acid storage tank consisting primarily of calcium sulphate enriched in radium.

Phosphoric acid produced by the reaction of phosphate rock with sulphuric acid contains fluorine as hydrogen fluoride (HF), fluosilicic acid (H_2SiF_6), fluorosilicate salts (especially salts of Na and K) and metal fluoride complexes involving Al and Fe, making it unsuitable for use in certain applications, such as the production of animal feed supplements. There are several methods for reducing the fluorine content, of which the easiest and cheapest is generally to add reactive silica (diatomaceous earth) to convert the fluorine compounds into SiF_4 while concentrating the acid in a forced circulation evaporator to expel HF and SiF_4 . Other methods of reducing the fluorine content include air stripping, steam stripping and concentration to superphosphoric acid followed by dilution back to orthophosphoric acid.

5.1.1.3. Management of residues

The scale removed periodically from the attack tank, which is predominantly non-radioactive, is transported by truck to the phosphogypsum stack.

Radium-bearing scale is removed from pipes, vessels and filtration equipment by abrasion or chipping and is usually sent to the phosphogypsum

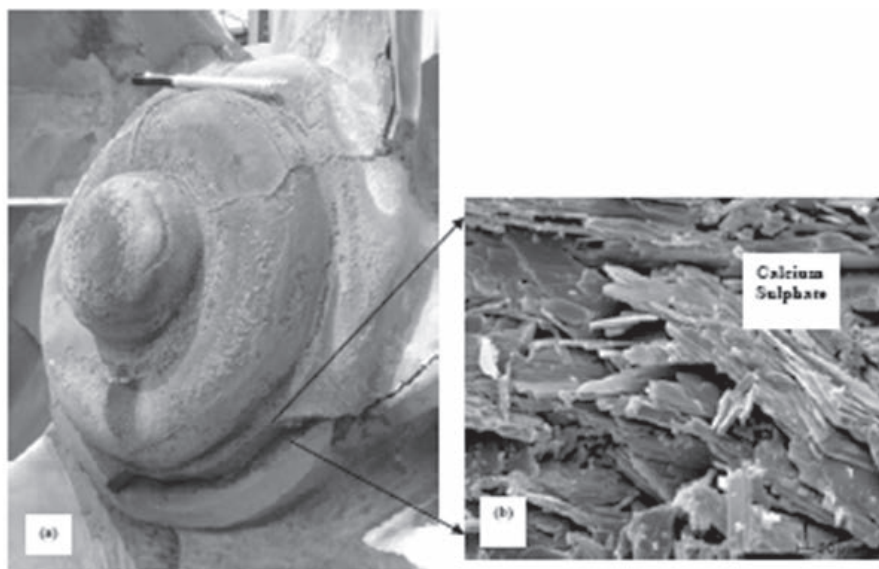


FIG. 21. Scale observed inside a green superphosphoric acid storage tank [68].

stack. The removal of scale in this way can cause localized site contamination that may subsequently need to be remediated. Alternatively, contaminated objects, particularly the filter pans and equipment, may be sent to off-site facilities for cleaning and refurbishing. This may result in the accumulation of radium-bearing scale at off-site premises.

The solid residues that settle out in the phosphoric acid clarification tanks are mixtures of very fine material comprising non-processed phosphate rock and non-filtered phosphogypsum [69]. They also contain fluosilicates and compounds of magnesium, aluminium and fluorine. This finding is supported by the following analytical results [70]:

- (a) The concentrations of trace elements and Fe in the residues are similar to those found in the phosphate rock.
- (b) The concentrations of Zn, Sr and Y are higher than the average values in normal sediments and soils.
- (c) Elevated concentrations of Ca (14.2%, 19.3%), S (8.2%, 10.7%) and P (6.6%, 13.5%) are found in residues from plants in Senegal and Morocco, respectively.

The residues are mostly recycled back to the attack tank or, in some cases, sent to the phosphogypsum stack.

When 40–55% phosphoric acid is purified using solvent extraction, the raffinate from the extraction process takes the form of a low grade acid containing the remaining P_2O_5 . It may be used as a fertilizer provided that its cadmium content, which can be as high as 60–100 ppm, does not exceed local legal limits. Solvents can be recovered from the raffinate and the purified acid and recycled back to the process.

The concentration of acid beyond 55% generates suspended solids containing more than 50% P_2O_5 . If these are removed, they are usually recycled back to the attack tank or used to make a low phosphate content fertilizer product such as MAP (see Section 6). Where a clarifier is used, the underflow may be sent to a filter and the phosphate-containing solids from this filter sent to the phosphogypsum stack. The solids that are separated out during the production of green superphosphoric acid also contain high concentrations of P_2O_5 . They are used in the manufacture of other end products such as MAP fertilizer.

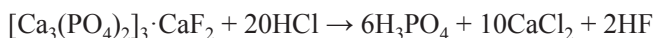
Rubber linings, where used, tend to become impregnated with radioactive material and are replaced periodically. The contaminated linings are sent to controlled disposal facilities specifically designed and authorized for the disposal of radioactive waste.

Process water used in various stages of the production process, including wastewater generated by the flushing of pipes, vessels and filtration equipment, is recycled by sending it to a large pond on the phosphogypsum stack for cooling and for settling or redissolution of solids before being returned to the process. Accordingly, process water is sometimes referred to as ‘pond water’.

5.1.2. Hydrochloric acid digestion

Processes have been developed in Israel and the USA for the production of high purity phosphoric acid by the acidulation of phosphate rock with hydrochloric acid, although only the Israeli process has been practised commercially [71]. These processes have limited application and their environmental impact is reported to be in need of consideration [72].

A detailed description of the Israeli process, shown schematically in Fig. 22, is given in Refs [45, 73]. The dissolution of phosphate rock by hydrochloric acid results in an aqueous solution of primarily calcium chloride and phosphoric acid and the emission of hydrogen fluoride, according to the reaction:



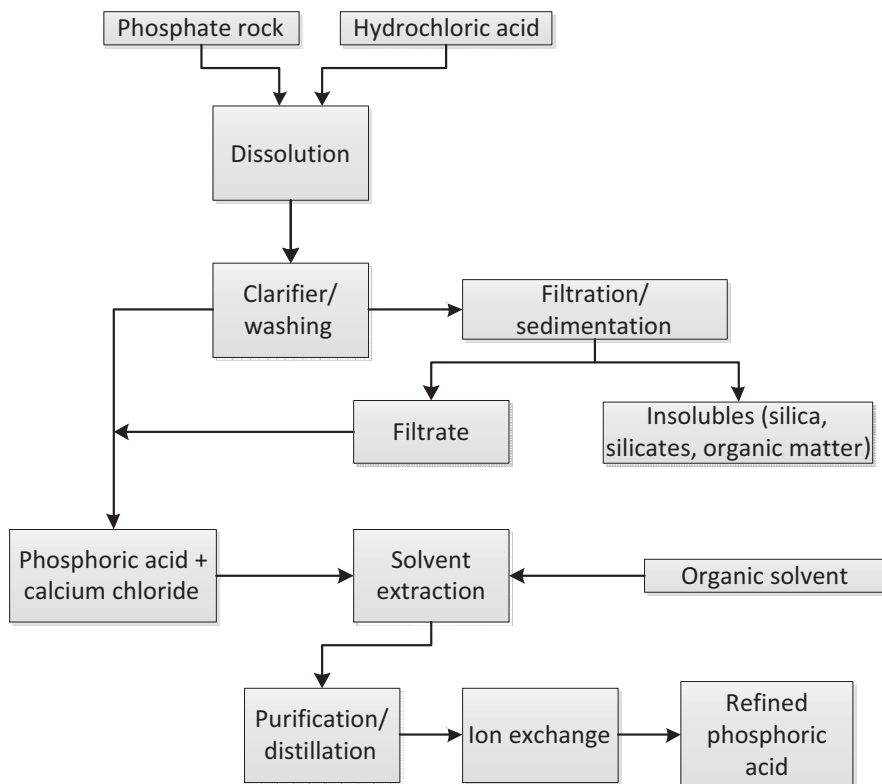


FIG. 22. Hydrochloric acid digestion process for the production of high purity phosphoric acid.

Other acid soluble components of the rock, such as CaCO_3 , decompose simultaneously. The small amount of insoluble residue remaining comprises primarily silica, silicates and insoluble organic matter. This residue can be separated by filtration or by sedimentation in a thickener, followed by washing. The choice of method depends on economic considerations and on the precise nature of the residue.

Phosphoric acid is then selectively extracted from the dissolution liquor using a countercurrent organic solvent extraction process, leaving a calcium chloride brine containing most of the impurities, such as iron and fluorine. The brine is stripped with steam to recover any dissolved solvent. The brine is either disposed of in the sea or on land, depending upon site specific economic and environmental considerations. The solvent, now loaded with phosphoric acid, also contains trace amounts of Ca^{2+} ions and other impurities and is further purified by multistage countercurrent contact with isoamyl alcohol, normal

butanol or a mixture of the two. The loaded solvent is then washed with a mixture of hydrochloric and phosphoric acids at controlled concentrations and stripped with water to recover the phosphoric acid. The stripped solvent, which is now almost completely acid free, extracts the remaining acids present in the raffinate and is recycled back to the extraction step. The phosphoric acid product contains some residual hydrochloric acid and dissolved solvent. The solution is concentrated to a P_2O_5 content of 69% in what is essentially a distillation process, during the course of which the residual hydrochloric acid and solvent are separated and recovered. The purity of the phosphoric acid so produced is much higher than that achievable from sulphuric acid digestion (see Section 5.1.1), although still not as high as that achievable from elemental (thermally produced) phosphorus (see Section 13).

5.2. RADIONUCLIDE ACTIVITY CONCENTRATIONS

5.2.1. Sulphuric acid digestion

Uranium is present in the phosphate rock primarily as the tetravalent ion U^{4+} and to a lesser extent the hexavalent ion U^{6+} . During the acid digestion process, ferrous iron readily reduces the U^{6+} present in the rock to U^{4+} . The reduction is also catalysed by fluoride ions originating from the rock. During acid filtration, contact with air results in oxidation to the hexavalent form and the uranyl ions complex mainly with phosphates. During the digestion process, 90–95% of the uranium in the phosphate rock migrates to the phosphoric acid [47], where it exists in the form of a uranyl phosphate complex and, to a lesser extent, uranyl sulphate and fluoride complexes. Uranium concentrations in phosphoric acid with a P_2O_5 content of 30% are given in Table 16 [45]. The remaining uranium in the phosphate rock migrates to the phosphogypsum, principally as a constituent of unreacted rock. Since ^{238}U and ^{234}U exist in the same chemical form, they remain in equilibrium during the digestion process.

Most of the radium in the phosphate rock migrates to the phosphogypsum. The exact amount depends on factors such as the process conditions and the characteristics of the phosphate rock. Percentages reported in the literature include 70–85% [47], 83.5% [74], 90% [75] and 92–93% [69]. Data on radioactivity levels in phosphogypsum are given in Section 10.3.

There are conflicting findings on the migration of lead during the digestion process. Some reports indicate that most or all of the lead in the phosphate rock migrates to the phosphogypsum, probably as poorly soluble lead sulphate [46, 76]. Other reports indicate that most or all of the lead migrates to the phosphoric acid [47, 75, 77].

TABLE 16. URANIUM CONCENTRATIONS IN 30% PHOSPHORIC ACID [45]

Country	Concentration of uranium as U_3O_8 (%)
Algeria	0.013
Brazil	0.008
Israel	0.0165
Jordan	0.0165
Morocco	0.014
Tunisia	0.008
USA:	
Florida	0.019
North Carolina	0.008

Most of the polonium in the phosphate rock migrates to the phosphogypsum. Percentages reported in the literature include 78% [75], 99% [47], 87–94% [69] and more than 99% [78].

As with lead, there are conflicting findings on the migration of thorium during the digestion process. The behaviour of thorium seems to depend strongly on the process conditions and the characteristics of the phosphate rock. Thorium forms sparingly soluble salts with hydroxides, fluoride and phosphate, while sulphate compounds are relatively soluble.¹⁶ Some studies have found that up to 75% of the thorium migrates to the phosphoric acid [79–81]. However, another study indicated that 80% of the thorium migrated to the phosphogypsum [75].

Radionuclide activity concentrations in phosphoric acid are given in Table 17. The ^{238}U activity concentrations vary over a wide range (0.14–2.6 Bq/g). The activity concentrations of ^{238}U can also be determined from the uranium concentrations in Table 16 by assuming that 1 g of U_3O_8 contains 12 347 Bq of ^{238}U . The activity concentrations determined in this way (in this case for 30% phosphoric acid) are similar to those reported in Table 17 but confined to a narrower range (1.0–2.3 Bq/g). The activity concentrations of radionuclides other than ^{238}U are, as expected, generally much lower.

Radionuclide activity concentrations in residues from phosphoric acid production are given in Table 18. In most cases, the activity concentrations are moderate (up to a few becquerels per gram). In some scales, however,

¹⁶ The predominant complexes are expected to be fluoride, phosphate and sulphate.

TABLE 17. RADIOACTIVITY IN PHOSPHORIC ACID (BY COUNTRY)

Location of plant	Phosphate rock feedstock		Activity concentration (Bq/g)								Reference
	Origin	Type	U-238	Th-230	Ra-226	Pb-210	Po-210	Th-232	Ra-228	Th-228	
Belgium	Not reported	Sedimentary and igneous	0.65		<0.005			<0.005			[85]
Morocco	Morocco	Sedimentary	0.74	0.16	—	0.005	0.001	0.001			[86]
Netherlands	Not reported	Sedimentary and igneous	1.4		0.074						[87]
South Africa	South Africa	Igneous	0.17 (0.14–0.19)		<LLD ^a	0.14–0.18 ^b		0.39 (0.28–0.47)	<LLD	0.25 (0.13–0.41)	[48]
Spain	Morocco	Sedimentary	1.07–1.83	0.1–0.2	0.006–0.008	0.078–0.109		0.01–0.05	<LLD	0.004–0.013	[46, 88]
Spain	Kola	Igneous	0.10–0.16	0.02–0.03	<LLD	<LLD		0.01–0.02	0.002	0.01–0.03	[46]
USA	Central Florida	Sedimentary	0.23–2.6	0.25	0.004–0.015			0.004			[16, 47]
USA	Northern Florida	Sedimentary	0.26		0.0074						[47]
Not reported	Morocco	Sedimentary	2.44 (2.28–2.58)		0.004–0.011						[74]

^a LLD: Lower limit of detection.^b Derived from values for phosphate rock (Appendix IV) and phosphogypsum (Appendix VI).

TABLE 18. RADIOACTIVITY IN RESIDUES FROM PHOSPHORIC ACID PRODUCTION

Residue	Location of plant	Type of feedstock	Activity concentration (Bq/g)						Reference
			U-238	Ra-226	Pb-210	Th-232	Ra-228	Th-228	
Scale:									
Attack tank	South Africa	Igneous	3.51	4.47		11.0	8.80	9.46	[48]
Attack tank	Northern Florida, USA	Sedimentary	0.14	0.83					[48]
Filtrate tank	Central Florida, USA	Sedimentary	1.0	14					[47]
Pipes, vessels, filters	Central Florida, USA	Sedimentary		3700					[82]
Washing acid section	Netherlands	Sedimentary and igneous		4-4000					[87]
Concentrator	South Africa	Igneous	0.079	0.086		0.983	0.424	1.48	[48]
Flash cooler	South Africa	Igneous	0.56	0.85		1.71	2.30	2.01	[48]
Circulation vessel	South Africa	Igneous	0.066	0.07		0.918	0.414	0.96	[48]
Phosphoric acid plant	UK	Sedimentary	<LLD ^a -2.84	0.03-2.42	0.19-4.55		Insignificant		[68]
Green superphosphoric acid plant piping	UK	Sedimentary	0.04-8.62	0.03-0.38	<LLD-0.12		Insignificant		[68]
Green superphosphoric acid storage tanks	UK	Sedimentary	0.21-0.48	5.27-11.11	0.96-11.55		Insignificant		[68]
Pipe scales	Spain	Sedimentary	0.98	1.41	2.03			0.02	[46]
Sediment, filtrate tank	Central Florida, USA	Sedimentary	<0.037	2.4-3.1					[47]
Sludge, filtration/washing	Huelva, Spain	Sedimentary	0.91-1.23	1.31-4.30	1.42-1.90	0.01-0.03	0.02-0.07	0.01-0.03	[88]
Filter cloths/residues	Huelva, Spain	Sedimentary	0.29-0.57	2.11-3.34	1.03-2.33			0.03-0.05	[46]
Raffinate	Not reported	Sedimentary and igneous	2.2	<0.005		0.08			[48]

^a LLD: Lower limit of detection.

^{226}Ra activity concentrations as high as 4000 Bq/g have been found. The activity concentration of ^{226}Ra in scale deposited on the internal surfaces of pipes, vessels and filtration equipment can reach as high as 3700 Bq/g [82–84].

5.2.2. Hydrochloric acid digestion

While this process has been well studied, little is known about the fate of the radionuclides introduced via the phosphate rock feedstock. The chemical conditions suggest that all the radionuclides, including uranium and radium, dissolve in the hydrochloric acid with only trace quantities remaining in the residue consisting of small amounts of silica, silicates and insoluble organic matter. The subsequent solvent extraction step is not likely to extract any of the radionuclides, leaving them in the calcium chloride raffinate. Radium, in particular, is chemically similar to calcium. However, even if the raffinate is evaporated to dryness, the radionuclide activity concentrations will be less than those in the phosphate rock feedstock because of the increase in mass. The phosphoric acid product is expected to contain negligible amounts of uranium and other radionuclides after the extraction and purification steps, but may contain some residual thorium.

In this process, hydrochloric acid is recovered from the phosphoric acid in the evaporators. Since radionuclides are dissolved in the hydrochloric acid, evaporators could be possible points of contamination, activity buildup and exposure. The mixing tanks used for recycling of hydrochloric acid could also be subject to contamination and activity buildup over time.

5.3. OCCUPATIONAL EXPOSURE

Most phosphoric acid production plants use the sulphuric acid digestion method and the information on occupational exposure given in this section is mostly related to this method.

5.3.1. Exposure pathways

The potential for significant occupational exposure occurs mainly in work activities associated with the handling of phosphate rock feedstock and the operation and maintenance of filtration equipment used for acid–phosphogypsum separation [89]. External exposure to gamma radiation is one of the main exposure pathways and is likely to be of concern in the following areas and activities:

- (a) Feedstock rock handling;
- (b) Attack tank mixing compartments and agitators;
- (c) Filtration equipment, in particular, scale laden pipes, distributors for rotating tilting pan filters and operating filter pans;
- (d) Acid clarification and storage, in particular, clarification and storage tanks containing settled sludge;
- (e) Equipment maintenance, in particular, exposure to radium rich scale during activities such as the replacement of pipes, the cleaning of evaporator heat exchangers, the repair of filter cloths and the mechanical removal of filter pan scale by chipping and abrasion.

The other main exposure pathway is via inhalation of radionuclides in airborne dust. This is likely to be of concern in the following areas and activities:

- (a) Feedstock rock handling;
- (b) Attack tank maintenance;
- (c) Filtration equipment during repeated filtration and washing;
- (d) Equipment maintenance, in particular, activities involving dry material such as filter pan scale chipping.

Exposure via the inhalation of radon is only likely to be of concern in highly enclosed and poorly ventilated areas in which process material is stored or handled. The tunnels within which phosphate rock is conveyed from storage areas to the processing plant ('rock tunnels') could represent such a situation if not adequately ventilated (see Table 11). In all other working areas, there is little potential for significant accumulations of radon to occur.

In the case of plants using the hydrochloric acid digestion method, exposures of workers are expected to occur mainly in the solid residue and scale handling areas.

5.3.2. Exposure levels

5.3.2.1. Gamma dose rates

Gamma dose rates during routine plant operation have been measured in workplaces at several phosphoric acid production plants and the reported values are summarized in Table 19. In most cases, the incremental gamma dose rates in phosphoric production plants in normally occupied areas are less than 0.2 $\mu\text{Sv/h}$ but may attain 2 $\mu\text{Sv/h}$ close to concentrated acid tanks or filtration systems.

Gamma dose rates can be higher during maintenance operations. The highest dose rates are likely to be those associated with the buildup of radium rich scale

TABLE 19. GAMMA DOSE RATES IN PHOSPHORIC ACID PRODUCTION PLANTS

Location	Average incremental dose rate (μSv/h)
Spain (during processing of rock from Morocco and Kola) [46]:	
Digestion area	0.03–0.06
Filtration system at washing steps	0.4–1.1
Milling area	0.02–0.4
Phosphoric acid concentration and storage areas	0.01–0.5
Islamic Republic of Iran (workplaces (measurements over a six month period using TLDs)) [90]	
	0.05–2.7
Poland (phosphoric acid production areas) [91]	
	0.08–0.24
Germany [87]:	
Several phosphoric acid plants	0.1–1.9
Production halls, acid collection tanks (worker occupied areas)	0.2

within equipment [92]. This occurs primarily in the phosphogypsum filtration system. In tilting pan filtration equipment, scale builds up in the pans, filter cloths, central filtrate distribution system and piping and can give rise to absorbed dose rates of up to 75 μGy/h on contact during normal operation [89]. Piping between the attack tank and the phosphogypsum filtration area can also accumulate radium rich scale [53]. Some of this piping can give rise to dose rates of 100 μSv/h, as measured on contact with the pipes in the maintenance workshops. Similarly, the filtration assembly, especially underneath the filters near the distribution hub, can produce dose rates on contact in the range 100–120 μSv/h during maintenance [92].

Gamma exposure data have been reported for maintenance activities in South African phosphoric acid plants processing phosphate rock of either igneous origin or 75% igneous and 25% sedimentary origin [48]. The results are summarized in Table 20. It is evident that the highest dose rates are those associated with maintenance work inside the flash coolers.

5.3.2.2. *Airborne dust*

Airborne dust measurements were carried out in a phosphoric acid plant in Huelva, Spain [93]. The ²³⁸U, ²³⁰Th and ²³²Th airborne activity concentrations

TABLE 20. EXPOSURE TO GAMMA RADIATION DURING PLANT MAINTENANCE ACTIVITIES [48]

Plant	Annual exposure period (h)	Average dose rate ($\mu\text{Sv/h}$)
<i>Attack tanks:</i>		
General internal maintenance	60	0.58
Manual scale removal	78	0.58
<i>Flash coolers:</i>		
General internal maintenance	16	1.5
Manual scale removal	48	1.5
<i>Concentrators:</i>		
General internal maintenance	70	0.58
Erection of internal scaffolding	10	0.4
<i>Circulating vessels:</i>		
Manual scale removal	16	0.5

were 0.3, 0.2 and 0.1 mBq/m^3 , respectively, for an average mass concentration of 0.37 mg/m^3 . Gross alpha and beta activity concentrations determined in airborne dust in phosphoric acid production plants in Florida, USA, are reported in Ref. [53]. The alpha activity concentrations were 40–70 mBq/m^3 . Airborne dust inhalation does not appear to be a significant exposure pathway in wet process phosphoric acid production facilities.

5.3.2.3. *Inhalation of radon*

Radon and radon progeny concentrations were measured in plants in Huelva, Spain [94] and in central Florida, USA [53]. Under normal operating conditions, concentrations were found to be similar to background levels. This included the rock tunnels at the plants in Florida, where the potential alpha energy concentration of radon progeny was found to be consistently less than $0.02 \text{ } \mu\text{J/m}^3$. The radon progeny concentration was also measured in rock tunnels under abnormal conditions, that is, after a long period with the ventilation fans not in operation. Although the potential alpha energy concentration was found to have increased, it still did not exceed $0.2 \text{ } \mu\text{J/m}^3$. Assuming an equilibrium factor of 0.4, this potential alpha energy concentration is equivalent to a radon gas

concentration of the order of 100 Bq/m³. Although this is higher than the worldwide average indoor radon concentration, it is not uncommon for such a level to be found in many homes and the occupancy period of the worker is, in any case, very short in comparison. Consequently, it can be concluded that the inhalation of radon is not a significant exposure pathway.

5.3.3. Effective dose

5.3.3.1. Gamma radiation

Most modern phosphoric acid plants incorporate a high degree of automation, which minimizes exposure periods in areas of high dose rates during normal operation. During maintenance operations inside process vessels, dose rates may be higher but, again, the annual exposure periods are short. Assessments of the annual effective doses from gamma radiation received by workers at various phosphoric acid plants around the world can be summarized as follows:

- (a) In central Florida, USA, doses were assessed using individual monitoring of workers by means of LiF TLDs and the more sensitive Al₂O₃:C OSLDs [53]. The radionuclide activity concentrations in the phosphate rock feedstock (of sedimentary origin) were about 1.4 Bq/g for the ²³⁸U decay series and less than 0.03 Bq/g for the ²³²Th decay series.
- (b) Doses received by workers at four phosphoric acid plants in Poland were assessed using a pressurized ion chamber and LiF TLDs deployed at fixed locations [91]. The phosphate rock feedstock was of sedimentary origin, imported from northern Africa (Morocco, Tunisia and Algeria), the USA and the Middle East. The activity concentrations of the radionuclides in the ²³⁸U decay series were typically about 1.5 Bq/g.
- (c) Doses were assessed using a gamma dose rate meter and measured occupancy periods at a plant in Spain. The plant was processing rock of sedimentary origin imported from Morocco and igneous rock imported from Kola, Russian Federation [46].
- (d) Doses received during maintenance work inside process vessels were assessed at plants in South Africa, using the average dose rates and annual exposure periods given in Table 20. The origin of the phosphate rock feedstock was either igneous or a mixture of 75% igneous and 25% sedimentary [48].

The results of these assessments, which are summarized in Table 21, suggest that the workers receiving the highest annual doses (up to 0.35 mSv)

TABLE 21. DOSES RECEIVED BY WORKERS FROM EXPOSURE TO GAMMA RADIATION IN PHOSPHORIC ACID PLANTS

Worker category	Mean annual effective dose (mSv)
<i>Workers handling phosphate rock feedstock:</i>	
Central Florida, USA [53]	0.194–0.300
Four plants in Poland [91]	0.05
<i>Phosphoric acid production workers:</i>	
Central Florida, USA [53]	0.264–0.348
Huelva, Spain [46]	0.135–0.212
<i>Maintenance workers, South Africa [48]:</i>	
General maintenance inside attack tanks	0.035
Manual scale removal inside attack tanks	0.045
General maintenance inside flash coolers	0.024
Manual scale removal inside flash coolers	0.072
General maintenance inside concentrators	0.041
Erection of scaffolding inside concentrators	0.004
Manual scale removal inside circulating vessels	0.008
Service workers working mainly off-site on the repair of pumps, filter pans and other equipment, central Florida, USA [53]	0.066–0.175

work in the attack tank and filtration areas. The doses received by workers engaged in the handling of phosphate rock feedstock are lower, while maintenance workers and service personnel receive the lowest doses.

5.3.3.2. Airborne dust

The dose from inhaled airborne dust was assessed during routine operation in a phosphoric acid production plant in the Islamic Republic of Iran [90] by air sampling and alpha activity measurements. The average internal dose for the plant was 0.14 mSv/a, with a range of 0.04–0.33 mSv/a across different workplaces. The maximum inhalation dose was found in phosphate rock bulk storage areas.

Results for phosphoric acid plants in Florida, USA, were published as dose distributions [53]. The most probable doses were <0.05 mSv/a for workers handling phosphate rock feedstock and <0.02 mSv/a for workers engaged in the actual phosphoric acid production process.

5.3.3.3. *Total effective dose*

Summing the dose values given in Sections 5.3.3.1 and 5.3.3.2 gives total annual effective doses of about 0.1–0.3 mSv for workers handling phosphate rock feedstock and 0.3–0.4 mSv for workers involved in the main phosphoric acid production process. For a plant in the Islamic Republic of Iran, the annual effective dose to workers, averaged over all workplaces, was 0.78 mSv.

Little information is available on doses received by workers in plants using hydrochloric acid digestion. The indications are that the doses from gamma exposures and radon inhalation are well below 1 mSv/a [95].

5.3.4. **Measures to reduce doses**

The undertaking of regular gamma surveys and the education of workers are examples of measures that, at a relatively low cost, have proven to be effective in ensuring that workers do not spend unnecessary time in areas of high gamma dose rates. Where the nature of the work requires workers to spend time close to high activity material such as radium rich scale in filtration equipment, the use of shielding has enabled doses to be reduced. Measures taken to minimize the formation of scale for purposes of maintaining plant performance (see Section 5.1.1.1) have the added advantage of minimizing workers' exposure to gamma radiation.

Various approaches have been used to minimize the doses received by workers via the inhalation of airborne dust. These include improvements in the design of process equipment, the adoption of measures to reduce the spillage of material and the installation of equipment to control airborne dust levels. The growing use of wet grinding of the phosphate rock feedstock instead of the more traditional dry grinding methods is particularly effective in reducing doses arising from dust inhalation, since wet grinding techniques do not generate any airborne dust. There is also no misting from wet grinding as it takes place inside the mill.

5.4. PUBLIC EXPOSURE

There is little potential for members of the public to receive significant exposures from phosphoric acid production facilities. The activity concentrations

in bulk materials are moderate and exposure to gamma radiation outside the site boundary can be expected to be negligible. Phosphoric acid plants are potential sources of airborne dust containing radionuclides. However, this dust tends to become rapidly deposited in the vicinity of the source and is unlikely to be transported to nearby residential areas. This has been confirmed by airborne dust monitoring around plants in central Florida, USA [96]. There is also little potential for public exposure via contamination of surface water bodies. Process water is generally recycled from the phosphogypsum stacking system back to the acidulation process. Normal environmental protection requirements will generally ensure that any water that is discharged from the facility is treated to reduce contaminant concentrations (including radionuclide concentrations) to acceptable levels.

The phosphogypsum stacks themselves are potential sources of public exposure. More details are provided in Section 10.4.

5.5. REGULATORY CONSIDERATIONS

Radionuclide activity concentrations in many of the process materials may exceed 1 Bq/g, with values sometimes reaching a few becquerels per gram in bulk materials (phosphate rock feedstock, phosphoric acid and phosphogypsum) and, occasionally, a few thousand becquerels per gram in the scale that accumulates inside pipes, vessels and filtration equipment. In terms of the Standards, therefore, wet process phosphoric acid production needs to be considered for regulation as a practice.

Evidence suggests, nevertheless, that doses arising from exposure to these materials are not high enough to be of serious concern. Annual doses received by workers are less than 1 mSv, while members of the public are unlikely to receive any significant dose. Consequently, it is expected that regulatory control would be limited to just a few basic requirements, with authorization in the form of a registration probably being the most appropriate regulatory option. During routine plant operation, the regulatory body would need to be satisfied that good OHS and environmental protection practices (including control of discharges) are being followed, that reasonable efforts are being made to ensure that doses remain below levels of concern and that exposure conditions in the workplace are reviewed as appropriate, for instance, if circumstances change. During non-routine operations, procedures would need to be in place to ensure that the doses received by maintenance workers, especially those engaged in the removal and handling of scale, remain below levels of concern. The scale itself would need to be disposed of at an approved hazardous waste facility.

With the exception of some of the scales removed from pipes and vessels during maintenance operations, the radionuclide activity concentrations in all the process materials are such that the Transport Regulations would not apply to these materials during transport.

6. MANUFACTURE AND USE OF AMMONIUM PHOSPHATE FERTILIZERS

Ammonium phosphates are a class of predominantly granular fertilizers produced by reacting phosphoric acid with ammonia. These fertilizers have a high nutrient content and convenient handling characteristics. They combine, in a single application, the two essential fertilizer ingredients, nitrogen and phosphate, in proportions favoured by the agricultural market and are referred to generically as NP fertilizers. The addition of potassium during the manufacturing process results in the production of NPK fertilizers. The favourable characteristics of ammonium phosphate fertilizers result in them being by far the most widely traded phosphate fertilizers worldwide [45]. There are two basic types of ammonium phosphate fertilizer:

- (i) MAP, typically containing 10–11% N and 50–52% P_2O_5 ;
- (ii) DAP, typically containing 18% N and 46% P_2O_5 .

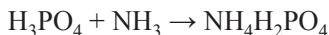
The primary emphasis of commercial production is increasingly on DAP.

6.1. PROCESS DESCRIPTION

6.1.1. Main process

MAP and DAP are produced by the reaction of phosphoric acid with ammonia. As phosphoric acid is tribasic (that is, having three replaceable hydrogen ions), it can form monoammonium, diammonium or triammonium phosphate salts, depending on the number of hydrogen ions replaced by ammonium ions (NH_4^+). Thus, the replacement of only one hydrogen ion produces MAP ($NH_4H_2PO_4$), while the replacement of two hydrogen ions produces DAP ($(NH_4)_2HPO_4$).

The primary reactions are:



and



Triammonium phosphate is unstable in ambient conditions, rapidly losing ammonia and reverting to the stable diammonium phosphate form. The production process for MAP and DAP fertilizer products consists of a ‘pre-neutralization’ step, using either a conventional reactor or a ‘pipe cross reactor’, followed by a granulation step. The ammoniation reaction is exothermic, with the reaction temperature reaching 115–120°C. During the granulation process, a potassium salt may be added, resulting in the production of NPK fertilizer.

In the conventional pre-neutralizer reactor method, ammonia (anhydrous liquid ammonia or, in some cases, ammonia gas or a gas–liquid mixture) is added to phosphoric acid, increasing the ammonia:acid mole ratio and causing the acid to become partially neutralized. Usually, 65–70% of the total phosphoric acid requirement is fed to the pre-neutralizer in the form of clarified acid (52–54% P_2O_5). The use of clarified acid ensures that it is free of any iron or aluminium phosphate impurities, these being undesirable because they cannot be ammoniated. The balance of the acid requirement may be provided in the form of relatively unclarified 28% P_2O_5 acid although, with a decline in quality of some phosphate rock feedstocks, clarified acid may be preferred in some situations. The balance of the acid requirement may also be provided in the form of scrubber liquor extracted from the scrubber system, containing 20–30% P_2O_5 . The degree of ammoniation is carefully controlled to produce a slurry with an ammonia:acid mole ratio of 0.5–0.7 for MAP production and 1.3–1.4 for DAP production.¹⁷ The slurry is then introduced to a granulator for further ammoniation and production of granular product (see Fig. 23). The slurry is distributed on a bed of recycled undersized ammonium phosphate product while the remaining ammonia required for completion of the reaction is introduced from below the bed. Granulation occurs by agglomeration and coating of the recycled MAP or DAP particles with the appropriate slurry. This final stage of the ammoniation reaction is controlled to a mole ratio of 1.0 for MAP production and 1.90–1.95 for DAP production.

¹⁷ In some facilities, MAP is produced by a ‘back titration’ method, in which a 1.3–1.4 mole ratio (DAP) slurry is first generated and then more acid is added to lower the ratio to the required 0.5–0.7 range.



FIG. 23. Rotary drum ammoniator–granulator (courtesy: Florida Industrial and Phosphate Research Institute).

As an alternative to the conventional pre-neutralizer reactor method, the pipe cross reactor method is being used to an increasing extent, since it offers various technical and commercial advantages, including reduced energy consumption. A length of pipe incorporating a pipe cross or pipe tee is installed within a rotary drum granulator. Ammonia is introduced into the cross or tee in the direction of the horizontal axis. Phosphoric acid is introduced through the mixer head in a direction perpendicular to the flow of ammonia. The reaction between the ammonia and the phosphoric acid is continued to the point of producing MAP, which is then discharged as a melt or slurry inside the granulator.

The granulated product, containing 2–3% water, is dried using hot air in a co-current rotary drum dryer. The dried product is then screened to separate out grains in the size range 1–4 mm. The precise size of grain produced depends on market requirements. The product is conveyed to a rotary drum cooler, where it cools from 70°C to about 40°C, and is then conveyed to a storage building. Oversize and undersize material from the screening step, together with residual on-size material, are recycled back to the granulator after pulverizing where necessary. In the



FIG. 24. Storage warehouse — product delivered by conveyor system (courtesy: Florida Industrial and Phosphate Research Institute).

post-granulation stage, the product is coated with, for example, vegetable oil to prevent airborne dust generation before being conveyed to the storage bins. In preparation for shipping, the granulated products are moved to storage areas by conveyors or by workers using large mobile equipment (see Figs 24 and 25). Workers collect spillages using smaller equipment or by hand with shovels. The products are shipped in bags, trucks, freight cars (see Fig. 26), barges or large ocean-going ships. MAP generally offers two NPK fertilizer grades: 11-52-0 and 10-50-0, the numerical values referring to the relative proportions of total nitrogen, minimum phosphate (as available P_2O_5) and potash (K_2O), respectively. DAP has a nominal NPK grade of 18-46-0. The fertilizers are applied to the soil using conventional dry fertilizer spreaders.

6.1.2. Management of residues

The production of fertilizer generates residues within the processing equipment. Typically, these are flushed out at intervals of 2–4 weeks and sent to



FIG. 25. Storage warehouse — payload for shipping (courtesy: Florida Industrial and Phosphate Research Institute).

the process water recycling system, which may form part of the water management system for phosphoric acid production.

There is always some spillage of dry product during production. While every attempt is made to return spillage to the production process, sometimes the presence of water makes this impractical. In that event, spillages are flushed with process water and the material sent to the process water recycling system. If the spill is large, it may also be transported by a separate vehicle or conveyor to the process water recycling system or to a nearby phosphogypsum stack.

Sources of gaseous emissions from the production of ammonium phosphate fertilizer include the reactor, granulator, dryer and cooler, as well as product sizing and material transfer operations [97]. Gaseous emissions are typically treated in the following manner, although variations exist from plant to plant:



FIG. 26. Loading of fertilizer product into a railcar (courtesy: Florida Industrial and Phosphate Research Institute).

- (a) The water vapour released during the ammoniation reaction, which accounts for a substantial portion of the water content of the slurry, contains gaseous ammonia, fluorides (such as hydrogen fluoride and silicon tetrafluoride) and ammonium phosphate particles. It is first passed through primary scrubbers that generally use weak phosphoric acid (20–30% P_2O_5) as the scrubbing liquor, principally to recover ammonia and particulates for recycling back to the process. It is then passed through secondary scrubbers that generally use recycled process water to remove fluorides. The effluent from the secondary scrubbers is returned to the process water recycling system.
- (b) Exhaust gases from the dryer and cooler, as well as those from product sizing and material transfer operations, also contain ammonia, fluorides and particulates. These streams are treated in the same way as those from the ammoniation reaction, except that they are first passed through cyclones to remove the majority of the particulates.

TABLE 22. RADIOACTIVITY IN AMMONIUM PHOSPHATE FERTILIZER

Material	Mean activity concentration (Bq/g)					
	U-238	Ra-226	Pb-210	Th-230	Po-210	Th-232
<i>MAP:</i>						
Central Florida, USA [16, 47, 98]	2.0–2.60	0.15–0.20		1.80		0.06
Western USA [98]	1.00	0.03				0.07
Tapira, Brazil [99]	0.61–1.16					0.20–0.22
Catalão, Brazil [99]	1.61–1.85	0.01				0.04–0.07
Brazil [100]	0.26–0.28	0.01–0.02	<0.02–0.04	LLD ^a –0.04		0.23–0.25
Germany [101]	2.00	0.10				
Huelva, Spain [102]	2.96	0.03	—	1.92	0.09	0.026
<i>DAP:</i>						
Central Florida, USA [16, 47]	2.60	0.15				
Northern Florida, USA [47]	0.94	0.02				
Western USA [98]	0.78	0.02				0.003
Huelva, Spain [102]	2.49	0.10		1.54	0.34	0.02
Germany [98]	2.20	0.02				0.02
Brazil [99, 100]	0.37–1.40	<0.005–0.01	<0.02			0.03–0.12
<i>Various NPK fertilizers:</i>						
Germany [50]	0.44	0.27				0.015
Belgium [50]	0.47	0.21				<0.015
Brazil [100]	0.27–0.35	0.42–0.45	0.53–0.64			0.08–0.30
Saudi Arabia [103]	—	0.003–0.28			0.005–0.11	0.002–0.074
Algeria [104]	1.0–1.28	0.13–0.19				0.12–0.13
Romania [105]	0.26	0.26				0.025
Huelva, Spain [102]	0.25–1.24	0.01–0.04		0.19–1.14	0.04–0.29	0.004–0.03

^a LLD: Lower limit of detection.

6.2. RADIONUCLIDE ACTIVITY CONCENTRATIONS

The phosphoric acid feedstock contains most of the uranium but very little of the radium originating from the phosphate rock (see Section 5.2). This radionuclide composition is reflected in the dry fertilizer products MAP and DAP [47]. Radionuclide activity concentrations in MAP and DAP dry product and NPK fertilizers are given in Table 22. The reported concentrations of ^{238}U in ammonium phosphate fertilizers produced in different countries generally lie in the range 0.3–3 Bq/g, but in most cases the activity concentration lies in the range 1–2 Bq/g. As expected, the concentration of ^{226}Ra is much lower and is in the range 0.01–0.1 Bq/g. The presence of low levels of ^{232}Th in MAP and DAP is also indicated. Some of the compound fertilizers with different NPK compositions manufactured by mixing with various proportions of potassium salts showed lower activity concentrations of ^{238}U , possibly due to dilution. However, a similar trend is not visible in the case of ^{226}Ra levels.

A comparison of the activity concentration in MAP and DAP bulk product and associated dust particles is given in Table 23. The ^{238}U , ^{226}Ra and ^{210}Pb radioactivity concentrations in bulk product and settled dust from central Florida, USA, are 2.33–4.15 Bq/g, 0.03–0.06 Bq/g and 0.25–0.33 Bq/g, respectively. No significant differences in the concentrations of ^{238}U and ^{226}Ra are found between dry product, settled dust and airborne particles. In the case of ^{210}Pb , however, elevated concentrations (up to 3.2 Bq/g) are found in airborne dust particles, probably due to the attachment of ambient airborne radon decay products.

6.3. OCCUPATIONAL EXPOSURE

6.3.1. Gamma radiation

Doses from external exposure to gamma radiation were assessed at fertilizer plants in central Florida, USA, using individual monitoring with LiF TLDs and $\text{Al}_2\text{O}_3\text{:C}$ OSLDs [53]. The plants produce mainly MAP and DAP, although a small amount of TSP was also produced. The mean annual effective dose was found to be in the range 0.081–0.171 mSv for workers in dry product areas and 0.122–0.197 mSv for workers in shipping and dispatch areas. Investigations have also been carried out at plants in Huelva, Spain, on exposure to gamma radiation and the annual effective dose was found to be in the range 0.076–0.134 mSv [102]. Doses received by workers as a result of external gamma exposure at a fertilizer plant in Poland were assessed using a pressurized ion chamber and LiF TLDs deployed at fixed locations [91]. The mean annual effective dose was found to be 0.10 mSv.

TABLE 23. ACTIVITY CONCENTRATIONS IN AMMONIUM PHOSPHATE FERTILIZER: COMPARISON OF BULK PRODUCT WITH DUST PARTICLES

Material	Mean activity concentration (Bq/g)		
	U-238	Ra-226	Pb-210
<i>MAP, central Florida, USA:</i>			
Bulk product	2.33	0.06	0.31
Settled dust	2.62	0.04	0.33
Airborne particles $\leq 100\ \mu\text{m}$	1.84	0.10	2.31
Airborne particles $\leq 10\ \mu\text{m}$	2.04	0.14	3.21
<i>DAP, central Florida, USA:</i>			
Bulk product	3.33	0.04	0.25
Settled dust	4.15	0.03	0.34
Airborne particles $\leq 100\ \mu\text{m}$	2.42	0.07	0.60
Airborne particles $\leq 10\ \mu\text{m}$	2.57	0.09	0.96
<i>DAP, northern Florida, USA:</i>			
Bulk product	0.94	0.02	
Airborne particles $\leq 100\ \mu\text{m}$	1.32	0.04	0.64
Airborne particles $\leq 10\ \mu\text{m}$	1.09	0.03	0.94

6.3.2. Inhalation of radionuclides in airborne dust

The inhalation of airborne dust is the predominant exposure pathway [46, 53]. The granulation process generates a considerable amount of dust in the form of crushed dry granulator material, leading to the possibility of this dust being inhaled by workers engaged in activities such as sampling, cleanup of spillage and manual handling. The application of an anti-dust coating to the product reduces the potential for dust generation during subsequent storage and shipping.

Detailed studies on particle size characterization of aerosols and experimental results on lung fluid solubilities have been reported from central Florida phosphate facilities [106–108]. Size measurements indicate that the aerosols do not follow a lognormal distribution and that the particle mass is increasingly concentrated in larger particle sizes in the granulation process locations. It was also noted that the values depend largely on mechanical disturbances by the movement of vehicles and other equipment, ventilation,

structure of the buildings and operational systems, including granulators, screeners, dryers and conveyors. The samples were collected using a multistage cascade impactor sampler and a high volume sampler at a flow rate of 1130 L/min. The mean airborne dust concentration in the granulation area was 7.2 mg/m³ and about 55% of the total mass was dominated by large (>20 µm) particles [107].

The lung fluid solubilities of uranium, thorium and lead in fertilizer dust particles (predominantly MAP and DAP) were measured using an in vitro technique involving simulated lung fluid with a neutral pH (7.2–7.4) matching that of the fluid lining the lung. Most of the phosphate, the main constituent of the dust particles, dissolved rapidly in the simulated lung fluid. However, uranium, thorium and lead dissolved less rapidly than the surrounding matrix [109]. The solubilities were found to be relatively independent of the product type or particle size. The most appropriate lung absorption classes determined from these lung solubility measurements were M for uranium and lead and S for thorium, according to the classification of lung absorption types by the ICRP [110]. The lung fluid solubility measurements were supplemented by additional measurements using a simulated lung fluid with an acidic pH (4.5–5.5) to match that of phagolysosomal fluid. The dissolution rate for ²³⁰Th under these more acidic conditions was found to be more than 300 times higher than that under neutral conditions. More details on the lung fluid solubility studies reported from the Florida phosphate industry are provided in Annex I.

Annual committed effective doses received by workers from the inhalation of airborne dust in plants in central Florida, USA, were assessed [109] using the ICRP respiratory tract model described in Ref. [37], the particle size measurements reported in Refs [106–108] and the lung solubility measurements reported in Ref. [109]. An annual exposure period of 2000 h was assumed.¹⁸ The results of the assessment are summarized in Table 24.

In phosphate plants in Poland, airborne dust concentrations have been reported as being quite high (3.0–13.5 mg/m³) [91]. These values were obtained from routine measurements at several locations, including phosphoric acid production and multi-compound fertilizer manufacturing plants. Although these dust concentrations were reported for both phosphoric acid and fertilizer plants, it is likely that they related mostly to fertilizer plants because of the dry nature of the process. Inhalation doses received by workers were assessed from the dust

¹⁸ This annual exposure period is very conservative, since a large portion of the working shift was reported to be spent in the control room or at some other non-dusty location. It has been suggested that a future dose assessment should be based on a more realistic annual exposure period of 500–800 h.

TABLE 24. DOSES RECEIVED BY WORKERS VIA INHALATION OF AIRBORNE DUST IN AMMONIUM PHOSPHATE PLANTS, FLORIDA, USA [53]

Work site	Mean annual committed effective dose (mSv)	
	Based on solubility in neutral simulated lung fluid	Based on solubility in acidic simulated lung fluid
Granulator area	0.14	0.25
Storage area	0.10	0.16
Shipping area	0.03	0.05

concentrations, assuming an AMAD of 1 μm . The radionuclide activity concentrations in the dust were not measured, but were, instead, estimated from the values measured for raw materials and fertilizers in the workplace. The assessed doses were in the range 2.9–5.6 mSv/a. It was reported that the lack of sufficient data for sensitive inhalation dose parameters had necessitated the application of conservative assumptions and probably resulted in the doses being overestimated.

6.3.3. Inhalation of radon

Radon concentration measurements have been made in plants in Huelva, Spain [94], and Florida, USA [53]. In all cases, the radon concentrations were at normal background levels. Consequently, inhalation of radon by workers is not regarded as a significant exposure pathway.

6.3.4. Total effective dose

The total annual doses received by workers in ammonium phosphate fertilizer plants can be estimated by summing the gamma doses reported in Section 6.3.1 and the dust inhalation doses given in Table 24. The results are given in Table 25 and show that a worker receives, at most, a dose of a few tenths of a millisievert per year.

TABLE 25. TOTAL DOSES RECEIVED BY WORKERS IN AMMONIUM PHOSPHATE FERTILIZER PLANTS, FLORIDA, USA

Work site	Total annual committed effective dose (mSv)	
	Minimum	Maximum
Dry product areas	0.22	0.42
Storage areas	0.22	0.36
Shipping areas	0.15	0.25

6.4. PUBLIC EXPOSURE

6.4.1. Fertilizer production

Public exposure may arise as a result of airborne dust emissions, disposal of spillages of solid material, storm water runoff contaminated by spillages and other inadvertent discharges caused by operating factors. These can be minimized by good housekeeping procedures, including, in particular, the prompt cleanup of spillages of process material. Control of spillage also brings economic benefit by retaining valuable product material. Provided that such measures are adopted, exposure of members of the public is likely to be insignificant.

6.4.2. Fertilizer use

As the use of fertilizer is subject to the requirements for existing exposure situations (see Ref. [2] and Section 3.1.1), agricultural workers exposed to phosphate fertilizer should be treated as members of the public. Exposures may vary widely from place to place depending upon the application rate of fertilizers and local environmental conditions. In an investigation carried out in Germany, the average dose received during the application of fertilizer was 0.6 $\mu\text{Sv/a}$ and the maximum likely dose was 4 $\mu\text{Sv/a}$ [59]. An investigation was also carried out in South Africa on the use of fertilizers produced from igneous phosphate rock [111]. A detailed assessment of the doses received by agricultural workers, considering all pathways of exposure, found that the doses never exceeded 10 $\mu\text{Sv/a}$, based on conservative assumptions, including worst case scenarios. Evidence suggests that public exposure attributable to the use of ammonium phosphate fertilizers is of no significant concern.

6.5. REGULATORY CONSIDERATIONS

The activity concentrations of radionuclides such as ^{238}U in both the phosphoric acid feedstock and the fertilizer product generally exceed 1 Bq/g. In terms of the Standards, therefore, the production of ammonium phosphate fertilizer needs to be considered for regulation as a practice. However, the evidence suggests that annual doses received by workers are consistently below 1 mSv and that there are no significant exposure pathways to members of the public. The most appropriate regulatory option for fertilizer production activities would seem to be either the granting of an exemption or a requirement for notification. This would be especially appropriate in situations where, as part of good industrial practice, basic OHS and environmental protection measures are in place, including measures for the management of process water, the containment of spillages and the control of airborne dust and discharges to the environment. The use of ammonium phosphate fertilizer does not need to be subject to any restrictions in terms of the requirements for existing exposure situations.

The radionuclide activity concentrations in the process materials and products are such that the transport of these materials would not fall within the scope of application of the Transport Regulations.

7. MANUFACTURE AND USE OF SUPERPHOSPHATE FERTILIZERS

Superphosphates represent a class of fertilizer product made by direct but partial acidulation of phosphate rock to render the phosphate mineral content largely water soluble. Various forms of insoluble apatite, which consist essentially of tricalcium phosphate, are converted to MCP using either sulphuric acid or phosphoric acid.

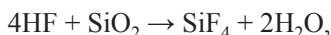
7.1. PROCESS DESCRIPTION

7.1.1. Single superphosphate (SSP)

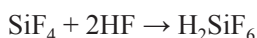
SSP (known also as ‘normal’, ‘simple’ or ‘ordinary’ superphosphate) is a mixture of (water soluble) MCP and CaSO_4 , with a P_2O_5 content of 16–22%. It is manufactured by reacting phosphate rock, usually a fluorapatite, with sulphuric acid. The basic chemical reaction is:



In contrast with the use of sulphuric acid digestion to produce phosphoric acid (see Section 5.1.1), the CaSO_4 produced by the digestion process is not separated out but, instead, remains as a component of the final product. There are many side reactions involving fluorine compounds, the most significant being:



and



The production process is, in principle, very simple and dates back to the 19th century. In modern SSP plants, the phosphate rock is processed by one of two methods:

- (i) The rock is dry milled to a particle size of 90–95% <150 μm and then reacted with 70–75% strength sulphuric acid in a high speed mixer; or
- (ii) The rock is wet milled and the resulting slurry is reacted with 98% strength sulphuric acid, the water content of the slurry causing the acid to be diluted within the mixer.

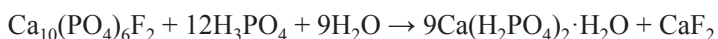
To facilitate completion of the reaction, a slight excess of sulphuric acid is used. The exothermic nature of the reaction raises the temperature to more than 90°C. From the mixer the slurry is sent to a ‘den’ where it solidifies on a travelling grate or rubber belt. The solid SSP is excavated 30 min to 4 h later, the exact period depending on the temperature, the reactivity of the rock and the degree of excess acid used. The excavated material is then processed in one of two ways to produce a final product that is uniform in composition and size:

- (i) The material is conveyed to a storage building (adequately ventilated to prevent the buildup of fluoride vapours), where the reaction continues for 2–6 weeks in a process called ‘curing’, after which the hardened and cured product is milled and screened before shipment as ‘powder SSP’; or
- (ii) The material is converted into a granular form using water and steam and then screened to separate out granules of the required size; oversize granules are milled and, together with the undersize granules, returned to the granulation step.

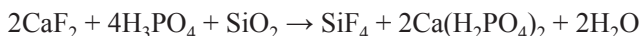
Most modern plants are completely mechanized. A typical production unit requires as few as two or three operators. Plants are generally regulated with regard to HF and SiF₄ emissions. By means of a water scrubber, HF generated by the acid digestion reaction and sometimes also fluoride vapours released within storage buildings are captured and returned with the scrubber water to the process water recycling system.

7.1.2. TSP

TSP consists entirely of MCP, with an available P₂O₅ content of 43–48%. It is produced by reacting phosphate rock (fluorapatite) with phosphoric acid (and sometimes sulphuric acid) and is manufactured in two basic product forms, the first being known as non-granular or ‘run-of-pile’ TSP (ROP-TSP) and the second as granular TSP (GTSP). The larger, more uniform particle size of GTSP gives it improved storage and handling characteristics. The basic chemical reaction is:



Side reactions involving fluorine compounds include:



and



The manufacturing process for ROP-TSP is similar to that for SSP (see Section 7.1.1). Phosphate rock and concentrated phosphoric acid (50–54% P₂O₅) are brought together in a cone or other high speed mixer, which discharges directly into a continuously moving ‘den’. A very dense slurry is produced, which, after solidifying into a porous, honeycomb-like mass, is pulverized by a rotary cutter into particles of various sizes. The particles are conveyed to the storage area for pile curing where the reaction continues for 3–5 weeks. The cured material is excavated and shipped as ROP-TSP or is converted into GTSP by treatment with water and steam in a granulator, followed by drying and screening.

GTSP is also manufactured directly by reacting milled phosphate rock with lower strength phosphoric acid (32–40% P₂O₅). The lower acid concentration allows the reaction products to be maintained in a fluid state throughout the mixing period of 1–2 h. The resulting slurry is mixed with a large amount of

dried, fine granules that have been recycled back from the product screening step. These granules become enlarged as a result of coating with the slurry. The coated granules are dried in a rotary dryer, with the heat of the dryer causing the chemical reaction to be accelerated towards completion. The dried granules are then sized using vibrating screens. Product size granules separated out by the screens are cooled in a countercurrent rotary drum or fluidized bed air cooler and then sent to a storage pile for curing. After a minimum curing period of 3–5 d, the granules are ready for bagging and shipping. Granules not meeting the size specifications are recycled back to the process (after crushing, in the case of oversize granules).

Residues accumulate in the processing equipment over time. These are removed periodically, typically every 2–4 weeks, and are sent to the process water recycling system.

Airborne particles are generated during the unloading, grinding, storage and transfer of ground phosphate rock and are controlled by air extraction systems and baghouse collectors. The baghouse cloth filters are reported to have removal efficiencies of over 99%. The collected particles are recycled back to the process. Gaseous fluorides (SiF_4 and HF) and airborne particles are generated by the acidulation reaction, although fluoride emanation from the storage pile in the curing building is relatively small because the acidulation reaction is, at that stage, almost complete. Airborne particles are also generated by the dryer, screens, cooler, mills and transfer conveyors. Emissions of fluorides and particles from the production area and curing building are controlled by scrubbing the off-gases with recycled pond water in cyclonic scrubbers. Emissions from the dryer, cooler, screens, mills, product transfer systems and product storage building are sent to a cyclone separator for removal of a portion of the dust before going to wet scrubbers to remove fluorides. Tail gas wet scrubbers perform final cleanup of the plant off-gases. The efficiencies of fluoride control are 90–99%, while an efficiency of 98% is achievable for particulate control. Used scrubber water is normally sent to the process water recycling system.

7.2. RADIONUCLIDE ACTIVITY CONCENTRATIONS

The reaction of phosphate rock with either sulphuric acid or phosphoric acid leading directly to a fertilizer product does not cause any of the radioactive material to precipitate selectively or concentrate in any manner. The radionuclide content of the fertilizer product reflects the combined radionuclide content of the phosphate rock and, where used, phosphoric acid [47]. Consequently, the activity concentrations of ^{238}U series radionuclides in SSP are all about 1 Bq/g, approximately 30% lower than those in the phosphate rock owing to the mass

increase from the addition of sulphuric acid. The ^{238}U activity concentration in GTSP is typically about 2.5 Bq/g, some 70% higher than that in the phosphate rock as a result of the addition of uranium via the phosphoric acid, while the ^{226}Ra activity concentration is about 1 Bq/g, approximately 40% lower than that in the phosphate rock. Given that the radionuclide activity concentrations in the phosphate rock and, where used, phosphoric acid are themselves quite moderate, the consequences of radionuclide dilution (SSP) or concentration (^{238}U in GTSP) are, for most rock sources, not of any great significance. Actual activity concentration data reported for several countries are given in Table 26.

7.3. OCCUPATIONAL EXPOSURE

Occupational exposures were investigated in four plants in Poland producing SSP, TSP and NPK fertilizers [91]. Doses from external exposure to gamma radiation were assessed using a pressurized ion chamber and LiF TLDs deployed at fixed locations. The mean annual effective dose from gamma radiation was found to be 0.05 mSv for the SSP plant and 0.20 mSv for the TSP plant.

TABLE 26. RADIONUCLIDE ACTIVITY CONCENTRATIONS IN SUPERPHOSPHATE FERTILIZERS

Material	Mean activity concentration (Bq/g)		
	U-238	Ra-226	Pb-210
<i>SSP:</i>			
Florida, USA [50]	0.74	0.79	
Belgium [50]	1.10	0.91	
Germany [50]	0.52	0.52	
Former USSR [50]		0.11	0.30
Poland [91]	0.78	0.91	—
Brazil [100]	0.41	0.87	1.25
<i>TSP:</i>			
Central Florida, USA [47, 50]	2.10	0.78	
Northern Florida, USA [50]	0.96	0.43	
Western states, USA [50]	1.60	0.52	
Germany [50]	0.80	0.23	
Poland [91]	1.79	0.86	
Brazil [100]	0.22	0.12	0.20

Inhalation dose assessments were carried out in phosphate fertilizer plants in Florida, USA [53]. Using various assumptions, the average annual committed effective dose from dust inhalation was conservatively estimated to be <0.05 mSv in the dry product areas and <0.8 mSv in the shipping and storage areas. These inhalation doses, although conservative, could be regarded as being reasonably representative of those received in SSP and TSP plants. Follow-up studies, aimed at removing the need for some of the conservative assumptions, indicated that the inhalation doses were likely to be lower, and well below 1 mSv/a [112].

7.4. PUBLIC EXPOSURE

7.4.1. Fertilizer production

During the fertilizer production process, it is evident that airborne emissions of fluorides and particulate matter are controlled very effectively. In addition, the small amounts of solid residues generated in these emission control systems and elsewhere are managed as part of the process water recycling system. It can be concluded that these pollution control measures will also be effective in controlling the release of radionuclides to the environment. Given that there are no other obvious exposure pathways to the public during the manufacturing process, it can be concluded that public exposure attributable to superphosphate fertilizer production is of no significant concern.

7.4.2. Fertilizer use

There is a potential for exposure of agricultural workers (who, in terms of the requirements for existing exposure situations [2], are regarded as members of the public) as a result of the use of superphosphate fertilizers. However, the lower activity concentrations in superphosphate fertilizers compared with those in ammonium phosphate fertilizers (see Section 6) suggest that the doses are likely to be insignificant.

7.5. REGULATORY CONSIDERATIONS

The activity concentrations of radionuclides such as ^{238}U in the phosphoric acid feedstock and in the GTSP fertilizer product generally exceed 1 Bq/g. In terms of the Standards, therefore, the production and use of superphosphate fertilizer needs to be considered for regulation as a practice. However, the annual doses received by workers are consistently below 1 mSv and there are no

significant exposure pathways to members of the public. The most appropriate regulatory option for superphosphate fertilizer production activities would seem to be either the granting of an exemption or a requirement for notification. This would be especially appropriate in situations where, as part of good industrial practice, basic OHS and environmental protection measures are in place, including measures for the management of process water, the containment of spillages and the control of airborne dust and discharges to the environment. The use of superphosphate fertilizer would not need to be subject to any restrictions in terms of the requirements for existing exposure situations.

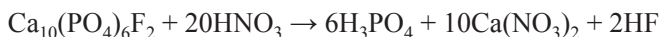
The radionuclide activity concentrations in the process materials and products are such that the transport of these materials would not fall within the scope of application of the Transport Regulations.

8. MANUFACTURE AND USE OF NITROPHOSPHATE FERTILIZERS (NITRIC ACID DIGESTION)

8.1. PROCESS DESCRIPTION

The treatment of phosphate rock with nitric acid using a process known as the ‘ODDA process’ produces phosphate fertilizer and calcium nitrate, which is also a fertilizer. The properties of the fertilizer products are such that they may not be as broadly competitive as other fertilizers, but their specialized nature has made them the subject of growing interest. Plants using this technology have operated in Finland, Germany, Italy, Netherlands, Norway, Romania and Sweden [113, 114]. Some plants in Pakistan also use this technology to produce nitrophosphate fertilizer [115].

The main reaction between nitric acid and phosphate rock is as follows:



After the separation of the insoluble material, phosphoric acid is neutralized with ammonia to produce a fertilizer. If the calcium nitrate is left in the solution, it reverts to dicalcium phosphate upon ammoniation as per the following reaction:

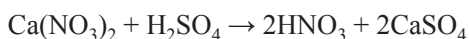


On heating the paste-like mixture to drive off the free moisture, the water solubility of the phosphate in the dried residue is greatly reduced due to the formation of dicalcium phosphate, as described by the following equation:



The nitric acid evolved during this step corresponds to approximately 25% of the nitric acid originally added. The dried product contains phosphate and nitrogen but the phosphate is of low solubility. The calcium nitrate content is sufficient to give the material undesirable hygroscopic properties and the sticky, pasty product is not well suited for shipment or for spreading as a dry bulk fertilizer [116, 117]. The properties can be improved by deep cooling the mixture and precipitating some of the calcium nitrate.

A more acceptable product is obtained if the mixture of phosphoric acid, calcium phosphate and calcium nitrate, with or without the partial removal of calcium nitrate, is treated with ammonia, although ammoniation causes the calcium to form a citrate soluble calcium phosphate [113] rather than the water soluble phosphates that are present in MAP or DAP (see Section 6). Dicalcium phosphate is usually insoluble in water but soluble in ammonium citrate solution and is, therefore, regarded as a source of ‘available’ P_2O_5 . However, fertilizer specification often requires water solubility and this type of product is limited to 50% water solubility of the P_2O_5 . The calcium can also be removed by precipitation with sulphate, the sulphate being added as sulphuric acid or ammonium sulphate [118], leaving only the phosphoric acid component of the mixture. The reaction with sulphuric acid produces nitric acid and phosphogypsum (calcium sulphate), according to the following reaction:



The nitric acid produced by the reaction may be recovered and recycled back to the process. However, as a means of producing phosphoric acid, the nitric acid process has no significant advantage over the more usual process involving the digestion of the phosphate rock with sulphuric acid.

A variety of fertilizers is produced from the addition of compounds such as calcium carbonate (lime), carbon dioxide, ammonia, potassium chloride or potassium sulphate. These include calcium ammonium nitrate, granular ammonium nitrate, granular ammonium sulphate with added potassium and various granular NPK products. A simplified diagram of the various process steps employed to produce ammonium nitrate fertilizers (calcium ammonium nitrate and NPK) is given in Fig. 27.

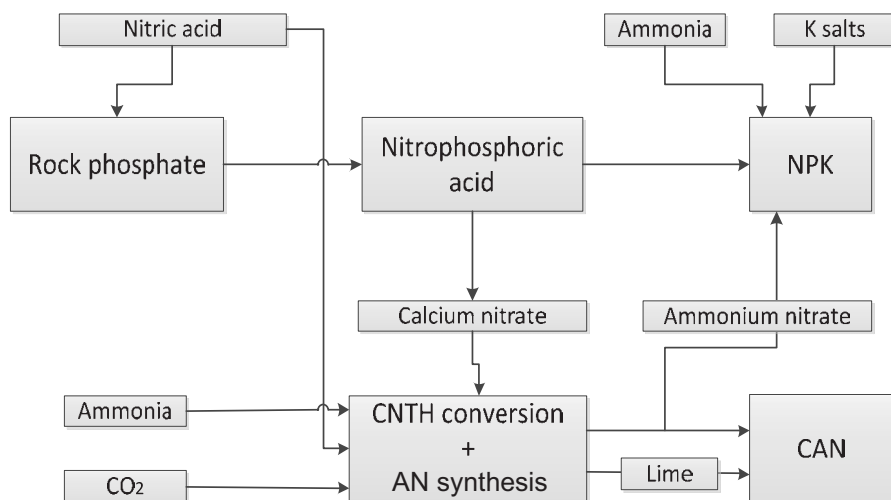


FIG. 27. Nitric acid route to nitrophosphate fertilizer production (CNTH: calcium nitrate tetrahydrate; AN: ammonium nitrate; CAN: calcium ammonium nitrate fertilizer; NPK: nitrogen–phosphorus–potassium fertilizer) [117].

The nitric acid processing route generates gaseous emissions of NO_x, NH₃ and HF to the atmosphere, as well as small amounts of silica (sand). Depending on radionuclide activity concentrations, the sand may be used for construction purposes.

8.2. RADIONUCLIDE ACTIVITY CONCENTRATIONS

All the radioactivity in the phosphate rock feedstock ends up in the fertilizer products, although at lower activity concentrations because of dilution due to the addition of nitric acid, ammonia and other compounds. The precipitation of calcium nitrate, where practised, does not affect this situation because the radioactivity remains with the phosphoric acid during the precipitation step. Should the calcium be precipitated by the addition of sulphuric acid, the phosphogypsum so produced would contain most of the radium but very little of the uranium. The actual activity concentrations reported from a few countries where nitrophosphate fertilizers have been produced are given in Table 27. The reported ²³⁸U activity concentrations are in a narrow range and typically about 0.4 Bq/g. One of the plants in Belgium produced nitrophosphate fertilizers for more than three decades and the typical radium activity concentration in the fertilizers never exceeded 0.1 Bq/g [95].

TABLE 27. RADIONUCLIDE ACTIVITY CONCENTRATIONS IN NITROPHOSPHATE FERTILIZERS

Country	Mean activity concentration (Bq/g)		
	U-238	Ra-226	Pb-210
Italy [114]	0.37	0.12	0.21
Belgium [95]		0.10	
Germany [50]	0.40	0.30	
Romania [105]	0.26–0.36	0.26–0.36	
Pakistan [115]		0.39	

8.3. OCCUPATIONAL EXPOSURE

Gamma dose rates have been measured in production areas and raw material and end product warehouses in a nitrophosphate fertilizer plant in Italy [119]. The dose rates in the production areas were 0.15–0.2 $\mu\text{Sv/h}$, comparable with background levels. Slightly elevated dose rates in the range 0.12–1.10 $\mu\text{Sv/h}$ were measured in the end product storage areas and were mainly due to the high percentage of ^{40}K present in the products. Data were also reported from the plant on the mass concentrations of airborne dust at several locations in the production areas and storage areas. The mean dust levels were in the range 0.1–2.1 mg/m^3 in the hoppers, reactors, granulation and other areas of the production unit. Higher levels of dust were found in the raw material warehouse and fertilizer product storage areas, where the mean concentrations were 5.4 and 1.7 mg/m^3 , respectively.

The annual effective doses received by workers from gamma radiation and inhalation of airborne dust reported in Ref. [119] are summarized in Table 28. These estimates are based on a conservative assumption of the periods spent by the workers in various work locations and probably reflect an upper estimate. Summing of the doses from external gamma exposure and inhalation of airborne dust gives total annual effective doses in the range 0.3–0.7 mSv.

Radon concentrations were also reported from the plant. Measurements showed radon concentrations to be in the range 40–60 Bq/m^3 in production areas, comparable with the natural background concentration at the site. However, elevated levels, up to 210 Bq/m^3 , were found in the raw material and end product warehouse, especially during the winter season.

TABLE 28. ESTIMATED DOSES RECEIVED BY WORKERS IN A NITROPHOSPHATE PLANT [119]

Work site	Mean annual effective dose (mSv)			
	Gamma radiation	Dust inhalation	Dust ingestion	Total
Raw material storage areas	0.4	0.04	0.006	0.45
Production area	0.3	0.03	0.01	0.34
Fertilizer product bagging	0.4	0.3	0.013	0.71
Pallet control	0.4	0.12	0.013	0.53
Product storage areas	0.6	0.13	0.013	0.74
Product bagging and warehouses	0.3	0.12	0.013	0.43

8.4. PUBLIC EXPOSURE

8.4.1. Fertilizer production

Using conservative assumptions, the maximum annual effective dose received by individuals living near a nitrophosphate fertilizer manufacturing plant in Italy was assessed [119]. The maximum annual inhalation dose from airborne dust was about 4 μ Sv, based on the predicted ground level air concentration at a distance of 0.2 km from the plant. The contribution of external gamma exposure was negligible at the site.

8.4.2. Fertilizer use

From the radionuclide activity concentrations reported in Table 27, it can be concluded that the exposure of agricultural workers (who, in terms of the requirements for existing exposure situations [2], are regarded as members of the public) as a result of the use of nitrophosphate fertilizers is of no significant concern.

8.5. REGULATORY CONSIDERATIONS

The activity concentrations of radionuclides such as ^{238}U in the phosphoric acid feedstock generally exceed 1 Bq/g, whereas in the nitrophosphate fertilizer

product, the activity concentration is below 1 Bq/g. In terms of the Standards, therefore, the production of nitrophosphate fertilizer needs to be considered for regulation as a practice. However, the evidence suggests that annual doses received by workers are consistently below 1 mSv and that there are no significant exposure pathways to members of the public. The most appropriate regulatory option for fertilizer production activities would seem to be either the granting of an exemption or a requirement for notification. This would be especially appropriate in situations where, as part of good industrial practice, basic OHS and environmental protection measures are in place, including measures for the management of process water, the containment of spillages and the control of airborne dust and discharges to the environment. The use of nitrophosphate fertilizer does not need to be subject to any restrictions in terms of the requirements for existing exposure situations.

The radionuclide activity concentrations in the process materials and products are such that the transport of these materials would not fall within the scope of application of the Transport Regulations.

9. MANUFACTURE AND USE OF ANIMAL FEED PHOSPHATES

The phosphate industry produces animal feed additives that contain various mixtures of phosphates and other nutrients, especially nitrogen, as well as micronutrients such as magnesium, sulphur and zinc. The phosphate content consists mainly of calcium phosphate in one form or another, with calcium being particularly effective as an animal feed supplement when used in conjunction with phosphorus. Since phosphate ores contain fluorine, which is toxic to animals, it is necessary to ensure that the fluorine content of the product is very low (less than 1% of the phosphorus content). Two basic types of animal feed phosphate are produced:

- (i) The first type contains tricalcium phosphate and is therefore marketed under the name TCP. It is also known as defluorinated phosphate rock. TCP is relatively high in calcium and derives its phosphorus content from a mixture of phosphate rock concentrate and phosphoric acid. It contains a minimum of 30% calcium and 18% phosphorus and can be represented by the chemical formula $\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Na}_3\text{PO}_4 \cdot \text{Ca}_2\text{SiO}_4$.

- (ii) The second type, the more popular of the two, contains MCP, dicalcium phosphate or mixtures of the two in various proportions. The products are marketed as a range of products referred to generically as MCP–DCP or ‘granular DCP’, or more specifically as MCP or DCP. These products are lower in calcium than TCP and derive their phosphorus content only from phosphoric acid or phosphate rock, depending on the production process used. Products marketed as MCP contain 15–20% calcium and 21% phosphorus, while products marketed as DCP contain 18–24% calcium and 18.5% phosphorus. MCP is also marketed as a fertilizer.

9.1. PROCESS DESCRIPTION

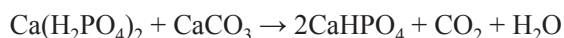
9.1.1. TCP animal feed

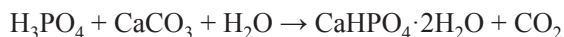
TCP is manufactured by mixing phosphate rock with phosphoric acid and sodium hydroxide and calcining the mixture at a temperature of 1370–1510°C. These conditions cause the fluorine in the feedstock materials to be driven off in the form of gaseous HF and convert the phosphate mineral into a biologically available form. Depending on the type of calciner used, steam may need to be added to facilitate the defluorination reaction. After cooling, the calcined material is granulated, dried and screened to produce TCP granules of the required size.

9.1.2. MCP–DCP animal feed

9.1.2.1. Reaction of phosphoric acid with limestone

Most MCP–DCP animal feed phosphates are produced by reacting defluorinated phosphoric acid (38–42% P_2O_5) with high quality finely ground limestone. Typically, the limestone contains 93–97% $CaCO_3$ and its particle size distribution is such that about 90% passes through a 200 Tyler mesh screen (0.075 mm). The neutralization of phosphoric acid with limestone can produce five different forms of calcium phosphate: $Ca(H_2PO_4)_2$; $Ca(H_2PO_4)_2 \cdot H_2O$; $CaHPO_4$; $CaHPO_4 \cdot 2H_2O$; and a crystalline product of variable composition having the X ray diffraction pattern of an apatite in which $Ca_3(PO_4)_2$ has been arbitrarily singled out from the hydroxyapatite family. The reactions with the limestone are as follows:





There is some evidence that, at moderate temperatures, the first solid to appear is dicalcium phosphate dihydrate. This hydrolyses readily to MCP monohydrate and tricalcium phosphate (apatite), according to the reaction:



In the presence of water, MCP monohydrate hydrolyses to give dicalcium phosphate and phosphoric acid, according to the reaction:

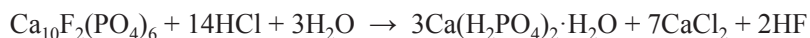


The reaction between the phosphoric acid and limestone is carried out in a high speed mixer followed by a granulator and is allowed to proceed nearly to completion in order to release as much carbon dioxide as possible. Material from the granulator is dried and then conveyed to sizing screens where it is separated into a product size fraction, an oversize fraction and fines. The oversize fraction is ground and, together with the fines from the screens and from the dust collection systems on the dryer, cooler and other equipment, is recycled to the granulator to provide seed nuclei for the granulation process. The on-size product from the screen is cooled and sent to storage.

A new method of producing dicalcium phosphate placed product on the market for the first time in 2009. The new method uses a previously unexploited part of the existing wet-acid process [120]. The conventional pre-release process for treating acidic water in phosphogypsum stacks by neutralizing the water using lime is not effective in removing phosphates. In the new treatment process, the phosphate content is recovered and used for producing dicalcium phosphate.

9.1.2.2. Reaction of phosphate rock with hydrochloric acid

MCP and DCP may also be produced by the acidulation of phosphate rock with hydrochloric acid. The reaction generates residues in the form of HF gas and a liquid effluent charged with CaCl_2 . For the production of MCP, the reaction proceeds as follows:



Excess calcium salts react with the liberated HF, resulting in the precipitation of insoluble CaF_2 . The effluent is discharged to surface water bodies after treatment. About 0.5 t of solid waste is produced per tonne of P_2O_5 . It is reported that this solid waste is deposited in stacks [85], as is the case with phosphogypsum.

For the production of DCP, phosphate rock is digested with hydrochloric acid repeatedly followed by decanting at each digestion step. The digested fraction of the phosphate rock is further treated with high quality limestone to precipitate the P_2O_5 from the solution. The white pulp generated is washed and vacuum filtered and the solid fraction is allowed to proceed to a drier to become DCP product. The liquid fraction, predominantly CaCl_2 effluent resulting from the filtration of the white pulp is released to a two or three step decantation and settling process and finally the residual water is treated in a water treatment facility before discharge. The undigested solid fraction is filtered and disposed of along with the water treatment sludge generated in the subsequent process steps. The liquid effluent obtained during the filtration of the sludge is usually sent to the water treatment facility where the effluent is treated along with the residual water from the DCP production line [25, 121].

9.2. RADIONUCLIDE ACTIVITY CONCENTRATIONS

It is reported in Ref. [25] that TCP contains ^{210}Pb and ^{210}Po each at an activity concentration of 0.1 Bq/g. In the case of MCP and DCP, the radionuclide compositions depend on whether production is by reacting phosphoric acid with limestone or by reacting phosphate rock with hydrochloric acid.¹⁹ Data on radionuclide activity concentrations in MCP and DCP are given in Table 29. With regard to the phosphoric acid route, the new DCP production method described in Ref. [120] reduces the ^{238}U and ^{226}Ra concentrations in the DCP product to only 10% of the levels found in DCP produced by the more traditional method.

In the production of DCP by the hydrochloric acid route, there is an inhomogenous distribution of uranium series radionuclides between the different process outputs. The radionuclides ^{238}U and ^{210}Pb dominate in the DCP product whereas ^{230}Th and ^{210}Po dominate in the solid wastes. Although the activity concentration of ^{210}Po in the DCP is initially lower in comparison with ^{210}Pb , this

¹⁹ The heavy metals content is also affected — the phosphoric acid route generally produces relatively high concentrations of Cd and other metals such as Mg, Al, Fe and Cr in the final DCP product, whereas the hydrochloric acid route leads to relatively high Pb and As concentrations.

TABLE 29. RADIOACTIVITY IN ANIMAL FEED PHOSPHATES

Material	Activity concentration (Bq/g)								Reference	Additional information	
	U-238	Th-230	Ra-226	Bi-214	Pb-210	Po-210	Th-232	Ra-228			Th-228
<i>Phosphoric acid + limestone process route:</i>											
MCP	0.11 (0.04–0.165)		<0.17		0.13		0.23 (0.07–0.426)	<0.27	0.179	[48]	Igneous feedstock, South Africa
DCP		1	<0.03		<0.03	<0.03				[25]	Sedimentary feedstock, Morocco
DCP	0.67		0.50	0.01	0.01					[120]	Sedimentary feedstock, central Florida, USA
DCP	0.06		0.05							[120]	Sedimentary feedstock, new production method
<i>Hydrochloric acid + phosphate rock process route:</i>											
MCP	1.57		0.014							[85]	‘Monocal-TCH’
MCP–DCP	2.47		0.010							[85]	‘Modical-TCI’
DCP	1.21		0.018							[85]	‘DCP-TCH’
DCP	2.06		0.016							[85]	‘Dical-TCI’
DCP	2.30		0.010							[85]	‘Dical-TCR’
DCP	0.95	0.01	0.015 ^a		0.17	0.35				[122]	Feedstock: 0.838 Bq/g U-238
DCP	1.5–1.7	0.1–0.4	0.1–0.2	2.0–2.1	0.1–0.8					[25,121]	Sedimentary feedstock, Morocco

^a It is reported that most of the Ra-226 migrates to the calcium chloride.

radionuclide grows back into equilibrium with ^{210}Pb after a relatively short time. The process generates two liquid effluents together with a sludge which is mainly the water treatment sludge [25]. The radionuclide activity concentrations in these process residues are given in Table 30. Radium, being chemically similar to calcium, forms RaCl_2 together with the CaCl_2 . The addition of BaCl_2 to the CaCl_2 effluent during the effluent treatment process will cause about 90% of the radium to precipitate as radium sulphate, which, together with BaSO_4 , will end up as part of the solid waste. The ^{226}Ra activity concentration in the solid waste is reported to be in the range 2–10 Bq/g [85]. If the effluent is not treated with BaCl_2 , the RaCl_2 will remain in solution during the effluent treatment process and will be discharged to surface water bodies along with the treated process water.

9.3. OCCUPATIONAL EXPOSURE

Most modern production facilities have a high degree of automation that makes it unnecessary for workers to spend much time in production areas. Gamma dose rates measured in a DCP production plant gave incremental dose rates in the range 0.1–0.2 $\mu\text{Sv/h}$ across different production locations. Annual effective doses received by workers through the gamma exposure pathway were estimated to be approximately 0.1 mSv [122]. Dust measurements were also reported from the plant. The main source of dust was identified as the product drying operation. Occasionally, dust was released from the containers feeding phosphate rock into the process tanks. The average dust concentration in the DCP production area was 3.5 mg/m^3 and the inhalation dose received by workers in that area was 0.07 mSv/a. It was concluded that dust could be a hazard in DCP manufacturing plants and that dust control measures and restrictions on periods of exposure to dust were important in reducing inhalation doses. Studies were also carried out to assess indoor radon in a DCP plant. No significant increase above the background levels was observed. For all exposure pathways, the annual effective doses received by workers were found to be much less than 1 mSv.

TABLE 30. RADIOACTIVITY IN RESIDUES FROM THE PRODUCTION OF DCP BY HYDROCHLORIC ACID DIGESTION OF PHOSPHATE ROCK [25]

Residue	Activity concentration (Bq/L)				
	U-238	Th-230	Ra-226	Pb-210	Po-210
Residual water			44–55		0.0061
Liquid effluent			9.1–20	0.006	0.008–0.04
Sludge	5.0–5.3	10.1–11.9	0.66–2.3	0.66–1.2	7.9–13

9.4. PUBLIC EXPOSURE

9.4.1. Animal feed production

Measurements of gamma dose rates and radon concentrations have been reported for four stack deposits containing solid waste associated with the production of MCP by hydrochloric acid digestion [85]. The results are given in Table 31. Assuming that the measurements were made close to the stacks (the distance is not specified), it is unlikely that any significant dose would be received by a member of the public living at a reasonable distance from the stacks. The results suggest quite strongly that, for the four stacks investigated, capping had no significant effect on radon exhalation. It is difficult to determine from the results whether capping had any significant influence on gamma radiation.

In a typical phosphoric acid and fertilizer production facility, any DCP production via the phosphoric acid route is generally a small part of the total production. As a consequence, the disposal of solid waste from DCP production into the phosphogypsum stack will have negligible impact on its radiological characteristics. A detailed study was performed to assess the radiological impact on the public arising from the disposal of solid waste from DCP production over a period of more than a decade [123]. The potential for remobilization of the radionuclides and their migration into freshwater systems, surface soils, fish, fruit and vegetables was examined and no enhancement in uranium series radionuclide concentrations was observed. The annual effective dose to the public from ²¹⁰Pb and ²¹⁰Po through the ingestion of food was estimated to be 0.03 mSv, which is comparable with the background levels in the region.

TABLE 31. EXPOSURE LEVELS AT WASTE STACKS ASSOCIATED WITH THE PRODUCTION OF MCP BY DIGESTION OF PHOSPHATE ROCK WITH HYDROCHLORIC ACID [85]

Stack volume (million m ³)	Ra-226 activity concentration (Bq/g)	Capping	Exposure level		Mean exposure level per unit Ra-226 concentration	
			Gamma dose rate (μSv/h)	Radon concentration (Bq/m ³)	Gamma dose rate (μSv/h)	Radon concentration (Bq/m ³)
0.1	3–4	No	1	60	0.3	17
0.5	3–4	Yes	1	30–85	0.3	16
0.1	2–4	Yes	0.05–0.25	30–80	0.1	18
1.4	3.5–10	No	2.6	50–200	0.4	19

9.4.2. Animal feed consumption

The use of animal feed containing radionuclides of natural origin is subject to the requirements for existing exposure situations [2]. In terms of these requirements, protective action in the form of restrictions on activity concentration might need to be considered, particularly if the reference level, typically a dose of 1 mSv/a to a member of the public, was exceeded. The activity concentrations of ^{238}U and ^{210}Pb in DCP produced via the hydrochloric acid route are elevated (see Table 29). Although DCP is diluted considerably when fed to animals, the extent to which ^{210}Pb (along with ^{210}Po , which grows back into equilibrium with ^{210}Pb) may enter the human food chain has been raised as a concern. An investigation of ^{210}Pb and ^{210}Po in chickens fed on a diet supplemented by DCP is reported in Refs [25, 121]. The chickens were fed on diets of 2.5% DCP (containing ^{210}Pb and ^{210}Po , each at an activity concentration of 0.06 Bq/g) and 5% DCP (containing ^{210}Pb and ^{210}Po , each at an activity concentration of 0.11 Bq/g). It was found that 95% of the ingested activity was excreted immediately. The remaining ^{210}Pb accumulated mostly in the bone, to an activity concentration of up to 0.012 Bq/g, while the remaining ^{210}Po accumulated in the liver (up to 0.05 Bq/g) and kidneys (up to 0.22 Bq/g). Modelling of the ingestion pathway for chicken consumption by humans gave a maximum ingestion dose of 0.011 mSv/a [25].

9.5. REGULATORY CONSIDERATIONS

Radionuclide concentrations exceeding 1 Bq/g may be found in the phosphoric acid feedstock, the phosphate rock feedstock (in TCP production), the solid waste (from the hydrochloric acid process route) and in some animal feed products. In terms of the Standards, therefore, the manufacture and use of animal feed phosphates needs to be considered for regulatory control as a practice. The results of dose assessments show that the annual doses received by workers and by members of the public do not exceed 1 mSv. However, control needs to be exercised over liquid discharges and the disposal of sludge residues. The most appropriate regulatory option for the manufacturing process would seem to be a requirement for authorization in the form of a registration. The consumption of animal feed phosphates does not need to be subject to any restrictions in terms of the requirements for existing exposure situations.

The radionuclide activity concentrations in the process materials and products are such that, with the possible exception of some solid wastes, the transport of these materials would fall outside the scope of application of the Transport Regulations.

10. PHOSPHOGYPSUM

10.1. INTRODUCTION

The digestion of phosphate rock with sulphuric acid generates the co-products phosphoric acid and phosphogypsum (see Section 5.1.1). For every tonne of P_2O_5 produced as phosphoric acid, 4–6 t dry mass of phosphogypsum is produced. The material mass ratio is even greater in practice because of the moisture content of phosphogypsum in its freshly processed state. For instance, phosphogypsum produced from the processing of Florida phosphate rock has a dry mass of about 5.2 t and a wet mass of 6.5 t for every tonne of phosphoric acid produced. The current annual production of phosphogypsum worldwide is about 160 million t, of which 40 million t (25%) is produced in the USA. Production is increasing worldwide and could reach 200–250 million t within the next decade or two. The total amount of phosphogypsum produced up to 2006 is estimated to have been about 6 billion t, of which 2.2 billion t (37%) was produced in the USA [33].

Depending on the particular wet process method employed (see Appendix V), phosphogypsum is produced in either the dihydrate form ($CaSO_4 \cdot 2H_2O$) or the hemihydrate form ($CaSO_4 \cdot \frac{1}{2}H_2O$). Dihydrate methods were generally favoured in the past, especially in the USA, but hemihydrate methods are now gaining in popularity since they produce phosphoric acid of a higher strength. In the presence of free water, the hemihydrate form will quite rapidly convert to the dihydrate form and, if left undisturbed, will settle into a relatively hard cemented mass.

From the initial adoption of the wet process, phosphogypsum has enjoyed a wide range of uses, especially in agricultural and construction applications. However, in view of the large quantities produced and the seasonal nature of agricultural demand, production has far exceeded demand, resulting in two main alternative management approaches for surplus phosphogypsum:

- (i) Stockpiling in large, above ground containment structures known as stacks (see Fig. 28), allowing the material to be used at a later time;
- (ii) Discharging to water bodies, usually large rivers, river estuaries or the sea, thus permanently disposing of the material.

Progressive changes in environmental regulation, notably within the European Union in the 1990s and more recently under the London Convention of the International Maritime Organisation [124], have largely brought the discharge of phosphogypsum to water bodies to an end, causing considerably more



FIG. 28. A phosphogypsum stack in central Florida, USA (courtesy: Florida Industrial and Phosphate Research Institute).

phosphogypsum to be stored on land. In addition, while the use of phosphogypsum continues in several parts of the world, concerns about its radioactivity content and, to a lesser extent, its heavy metals content, have led to restrictions on the use of phosphogypsum in some markets, even though such concerns do not always have a proper scientific foundation. This has resulted in phosphogypsum stacks being, in effect, turned from short term holding piles into long term disposal facilities [125]. It has been estimated that, by 2006, a total of 2.6–3.7 billion t of phosphogypsum had been accumulated in stacks worldwide, representing 44–62% of the total amount of phosphogypsum produced up to that time. The corresponding figure for the USA (mostly in Florida) was 1.7 billion t, representing approximately half of the worldwide total. An overview of what has happened to all the phosphogypsum produced up to the year 2006 is given in Table 32. In estimating the amounts involved, a significant level of uncertainty relates to countries outside the USA concerning the amounts of phosphogypsum discharged, used or abandoned relative to the amount retained in stacks. Consequently, two estimates for these countries are given in Table 32. In the ‘minimum stockpile’ estimate, it is assumed that the amount of phosphogypsum that has been discharged is at the upper bound of the estimated range and that 25% of the remaining phosphogypsum has been used or abandoned, both assumptions leading to a minimum estimate of the amount stockpiled. In the ‘maximum stockpile’ estimate, it is assumed that the amount discharged is at the

TABLE 32. CUMULATIVE AMOUNTS OF PHOSPHOGYPSUM UP TO 2006

Location	‘Minimum stockpile’ estimate		‘Maximum stockpile’ estimate	
	Amount (billion t)	Proportion of total (%)	Amount (billion t)	Proportion of total (%)
<i>Stockpiled in stacks:</i>				
USA	1.7	29	1.7	29
Other countries	0.9	16	2.0	34
Total	2.6	44	3.7	62
<i>Discharged to water bodies:</i>				
USA	0.5	8	0.5	8
Other countries	2.5	42	1.3	21
Total	3.0	50	1.8	29
Used or abandoned	0.3	5	0.5	8
Total amount produced	6.0	100	6.0	100

lower bound of the estimated range and that only 20% of the balance has been used or abandoned, both assumptions leading to a maximum estimate of the amount stockpiled.

Phosphogypsum is currently being added to stacks at an annual rate of about 40 million t in the USA and 90 million t elsewhere. At these rates, the total amount of phosphogypsum stored in stacks will more than double to 7–8 billion t by 2040. Most of this growth will occur in countries with developing economies, where a three- or fourfold increase can be predicted from current growth patterns. The actual growth is likely to be faster because of further reductions in discharges to water bodies and increased phosphogypsum production. Assuming a complete cessation of discharges to water bodies and an increase in phosphogypsum production from 160 to 240 million t per year, the projected total of 7–8 billion t would be reached by 2025, that is, 15 years earlier.

In addition to the phosphogypsum itself, very large volumes of highly acidic process water (also known as pond water) are associated with phosphogypsum production. Billions of litres of this water are stored on top of, and in, active stacks (see Fig. 29).



FIG. 29. Storage of process water on a phosphogypsum stack at Huelva, Spain.

The indefinite stacking of phosphogypsum has negative impacts in terms of the engineering and environmental aspects of the stacks themselves and the associated costs and long term liabilities [83, 126]. These negative impacts were not fully appreciated in the past, but awareness of them has been growing for some time. A good example of this can be found in the USA, where the costs of closing certain older phosphogypsum stacks under locally binding regulations [127], notably in central Florida, have become very high, not least because the stacks were not designed and constructed in accordance with current standards and the use of liners to prevent groundwater contamination was not yet mandatory [128]. Furthermore, the costs of closure have fallen on taxpayers rather than on the owning companies because the stacks in question had been abandoned after the companies went into liquidation [33]. As a result, new stacks either have to be reported as liabilities in the financial statements of the owning company or subject to a minimum bond of US \$150 million to cover the costs of future closure and ongoing maintenance.

This awareness of the negative impacts of indefinite stacking and the huge increases in the amounts of phosphogypsum having to be stored in stacks in the future have highlighted the need for a systematic reappraisal of the merits of, and potential for, increased use of phosphogypsum worldwide. At present, the use of phosphogypsum accounts for only a very small proportion of the amount



FIG. 30. Phosphogypsum.

produced (probably much less than 5%). In addition, attention is now being drawn to the potential benefits that might be derived from innovations in wet process phosphoric acid production that could reduce the operational requirements for stacks and the large ponds associated with them.

10.2. PHYSICAL AND CHEMICAL PROPERTIES

Phosphogypsum is a damp, silty or silty sand sized material (see Fig. 30). Dihydrate phosphogypsum consists primarily of silt size, relatively soft aggregates of crystals, the morphology of which depends on the source of the phosphate rock and the reaction conditions in the attack tank. The maximum particle size varies from approximately 0.5 mm (no. 40 sieve size) to 1.0 mm (no. 20 sieve size) and typically 50–75% of the material passes through a 0.075 mm (no. 200 sieve size) screen. The silty size range of dihydrate phosphogypsum classifies it as an A-4 soil in the AASHTO²⁰ soil classification system [129].

²⁰ AASHTO: American Association of State Highway and Transport Officials.

Hemihydrate phosphogypsum generally has a larger particle size than the dihydrate form.

The moisture content is usually in the range 8–30%. For maximum density, the optimum moisture content of phosphogypsum (dihydrate or hemihydrate) lies in the range 15–20% [130]. Typical engineering properties of phosphogypsum such as density, strength, compressibility and permeability (hydraulic conductivity) can be found in Refs [130–132]. These properties are influenced not only by the characteristics of the source rock and the reaction process, but also by the method of deposition, age, location and depth within the stack in which the phosphogypsum is found. Owing to the homogeneous nature of phosphogypsum particles, the stacking process causes the material to become compacted over time. Thus, the density and strength of the material generally increase with the age of the stack and the depth within the stack, while the compressibility and permeability are likely to show a corresponding decrease. However, this effect may be compromised by the presence of voids created by dissolution channels and cavities caused by rainfall infiltration. The specific gravity of phosphogypsum produced in Florida, USA, is typically 2.3–2.6, while the upper bound of the range of dry densities is likely to lie in the range 1.47–1.67 g/cm³, based on standard Proctor compaction (a laboratory method to determine, experimentally, the dry densities of soil) [130]. Values for phosphogypsum produced elsewhere may be slightly different. The addition of fly ash or Portland cement to phosphogypsum yields a mixture known as stabilized phosphogypsum that has slightly higher values of maximum dry density and optimum moisture content [133].

In terms of shear strength, phosphogypsum in its unconsolidated, undrained and unstabilized form typically exhibits an average internal friction angle of 32° and a cohesion value of 125 kPa. For cement stabilized phosphogypsum, the corresponding values are 28–47° and 76–179 kPa, respectively [134]. Unstabilized phosphogypsum has a permeability coefficient of $2.1\text{--}13 \times 10^{-5}$ cm/s.

In addition to calcium sulphate, the main constituent, phosphogypsum contains alkali fluosilicates (Na_2SiF_6 and NaKSiF_6), chukhrovite ($\text{Ca}_4\text{SO}_4\text{SiAlF}_{13} \cdot n\text{H}_2\text{O}$) — a complex iron phosphate ($\text{Fe}_3(\text{NH}_4, \text{K}, \text{H})\text{H}_8(\text{PO}_4)_6 \cdot 6\text{H}_2\text{O}$), the majority of which is in the ammonium form — and many other possible compounds [135]. A comparison of the major constituent concentrations in phosphogypsum with those in the phosphate rock from which it is derived helps to determine the effectiveness of the sulphuric acid digestion process. A knowledge of these concentrations can also be useful in matching phosphogypsum types to end uses, especially in agricultural applications where specific nutrients, such as zinc, within the phosphogypsum can be used to remedy specific soil deficiencies [136]. Published data on the main chemical constituents of phosphogypsum are given in Appendix VI. Obviously, calcium and sulphate are the major constituents and

together they account for up to 92% of the total content. Analyses have indicated the presence of sodium, magnesium, aluminium and iron, apart from silica and P_2O_5 . The silica content of phosphogypsum is 0.5–18%, depending upon the rock source and the efficiency of the wet process. Phosphogypsum also contains fluorides, at concentrations of 0.1–1.8%. Fluoride concentrations may be significantly reduced by effective washing of the phosphogypsum before use or disposal. Since calcium sulphate is the major constituent, phosphogypsum is acidic in nature and the acidity is increased further as a result of contamination with residual phosphoric, sulphuric and hydrofluosilicic acids. For instance, phosphogypsum produced in the USA has pH values in the range 2.5–6. The aim is for most of the P_2O_5 in the phosphate rock feedstock to be recovered as phosphoric acid and, in pursuit of this aim, the trend is towards reduced amounts of residual P_2O_5 within the phosphogypsum. Nevertheless, phosphogypsum may still contain 5–20 times more phosphorus than is present in natural soils and sediments.

A knowledge of the concentrations of impurities in phosphogypsum can be important for defining technical solutions for the production of a marketable product and the consequent management and environmental policies for its storage in stacks. The concentrations of most trace elements in phosphogypsum are significantly lower than those in the source rock, even after allowing for the fact that the digestion of 1 t of rock typically produces 1.46 t of phosphogypsum. This implies that the trace elements tend to migrate with the P_2O_5 fraction to the phosphoric acid. Small amounts of radioactive elements, such as radium and uranium, and of (non-radioactive) heavy metals, such as arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver, as well as phytotoxic fluoride and aluminium, are present in phosphogypsum and its pore water [76]. The concentrations of these impurities vary widely, depending on the composition of the phosphate rock used as feedstock [75, 78] and, to a lesser extent, on other factors, such as differences in operation of the processing plant [137]. With some exceptions, the concentrations of cadmium and other heavy metals in phosphogypsum derived from igneous phosphate ore tend to be lower than those in phosphogypsum derived from sedimentary ore, while the concentrations of lanthanides (rare earth elements) tend to be higher. Published data on heavy metal concentrations and rare earth elements in phosphogypsum are given in Appendix VI. It has been observed that heavy metals tend to concentrate in particles smaller than 20 μm , and it is in this size fraction that the most significant variations in concentration are to be found, depending on the characteristics of the source rock [138, 139].

10.3. RADIONUCLIDE ACTIVITY CONCENTRATIONS

All the constituent minerals in phosphogypsum listed in Section 10.2, especially the main constituent, calcium sulphate, can be expected to exhibit radionuclide substitutions. The primary substitution compounds are thought to be sulphates in the form of radium sulphate, lead sulphate, lead disulphate, polonium disulphate and thorium disulphate. The mineral chukhrovite ($\text{Ca}_4\text{SO}_4\text{SiAlF}_{13} \cdot n\text{H}_2\text{O}$), a constituent of phosphogypsum, is known for having a relatively high radium content owing to the substitution of radium for calcium [17]. The radionuclides known or suspected of concentrating in phosphogypsum can also form fluorides, oxides, hydrides and sulphides.

A small amount of uranium in the U^{4+} ionic form migrates to the phosphogypsum owing to four main reasons:

- (i) Unreacted rock particles containing U^{4+} become coated with phosphogypsum;
- (ii) Some substitution by U^{4+} occurs in the crystal lattice of phosphogypsum;
- (iii) Residual amounts of phosphoric acid, containing uranium phosphate, remain with the phosphogypsum after filtration and transport to the stack;
- (iv) U^{4+} may adsorb on to the surface of phosphogypsum as UO_2HPO_4 .

The residual phosphoric acid remaining with the phosphogypsum may also contain a small amount of uranium in the form of uranyl ions (UO_2^{2+}). Moreover, substitution of Ca^{2+} ions by uranyl ions may occur on the surface of the phosphogypsum crystal lattice [140].

Data on radionuclide activity concentrations in phosphogypsum are given in Appendix VI. The activity concentrations of ^{238}U are mostly below 0.1 Bq/g, with occasional higher values possibly indicative of lower recovery levels of phosphate in the attack tank due to some degree of inefficiency in the process. The activity concentrations of ^{226}Ra and its progeny are generally in the range 0.2–3 Bq/g for material derived from sedimentary phosphate ore. The ^{226}Ra concentrations in phosphogypsum derived from igneous ore are lower, ranging from less than 0.01 to 0.7 Bq/g. The worldwide distribution of ^{226}Ra activity concentrations, estimated by fitting a lognormal curve to the available data, is shown in Fig. 31. The arithmetic mean of the distribution is 1 Bq/g. Activity concentrations vary between stacks and even between different levels in stacks, depending on factors such as age and source rock characteristics.

There is potential for the removal of some of the radionuclides from phosphogypsum while it is still in slurry form. Reduction of the radionuclide content using a cyclone has been attempted on the basis of indications that a higher proportion of the radioactivity is to be found in the fine fraction, although

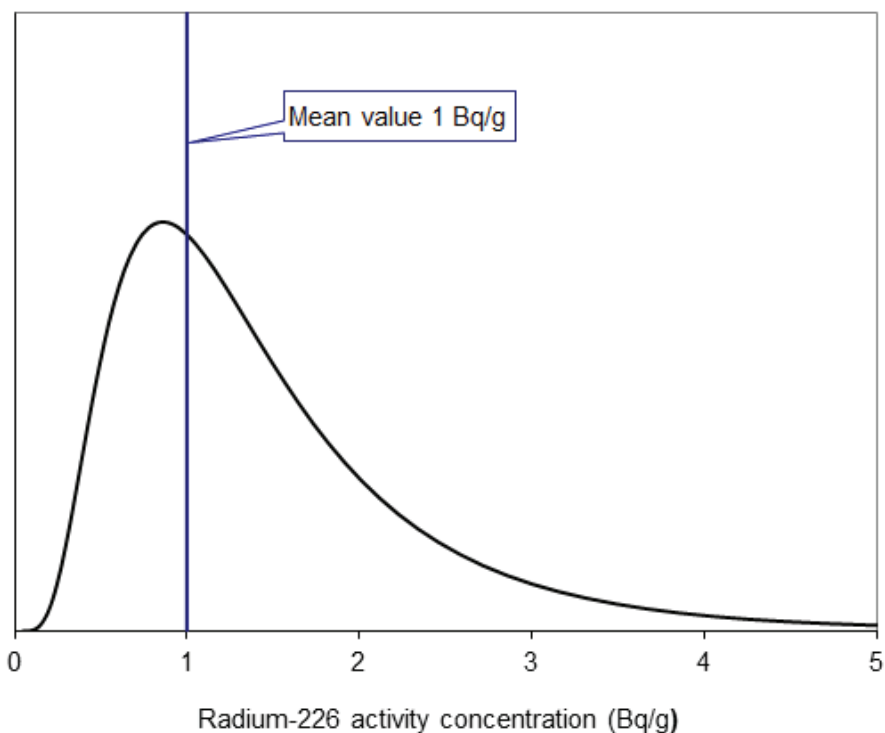


FIG. 31. Estimated worldwide distribution of ^{226}Ra activity concentrations in phosphogypsum.

this is not supported by more recent data [141]. The sulphates of radium and calcium differ in ionic radius, crystalline structure and solubility (calcium sulphate is slightly soluble and radium sulphate is highly insoluble) [142] and thus would not be expected to co-crystallize.

Any large scale radiochemical purification of phosphogypsum is dependent on economic factors. A process known as the Merseberg ammonocarbonation process yields ammonium sulphate, an excellent fertilizer, and calcium carbonate, a useful product for neutralization of acidic water. This process has been used on a commercial scale in China, India and Indonesia. Almost all the radioactivity within the phosphogypsum migrates to the calcium carbonate, leaving the ammonium sulphate fertilizer product lower in radioactivity than most natural materials. However, the process has enjoyed only limited use because of abundant supplies of inexpensive ammonium sulphate from other industries.

10.4. STORAGE OF PHOSPHOGYPSUM

The amounts of phosphogypsum stored in stacks are vast (approximately 3 billion t worldwide). There are stacks of various sizes in well over 50 countries, of which the largest cover land areas measured in square kilometres. In Florida, USA, for instance, there are some 25 stacks covering a land area of more than 50 km² [143], implying an average area of more than 2 km² per stack. The management of phosphogypsum stacks requires care because of the large volumes and land areas involved, the potential for emissions of dust and radon gas to the atmosphere and the potential for seepages containing fluorides, heavy metals (such as cadmium) and, to a lesser extent, radionuclides. The management approach for phosphogypsum stacks is no different in principle from that for engineered structures containing other types of NORM in bulk amounts, such as residues (tailings and waste rock) from the mining of radioactive ores. This management approach is described in Ref. [5]. The following basic measures help to mitigate or prevent any negative impact:

- (a) The provision of perimeter systems to contain possible leaks or spills;
- (b) The use of suitable liners to prevent contamination of groundwater [144];
- (c) The provision of a well-maintained water cover to reduce airborne emissions of dust and radon gas;
- (d) The provision of a system of dust suppression in the case where it is not feasible to provide a water cover, either by keeping the material wet or by planting grass or other light vegetation (although the establishment of vegetation may increase the rate of radon emission).

There are two methods of stacking: wet stacking and dry stacking. The wet stacking method is the more common of the two. It is used by most of the plants that produce dihydrate phosphogypsum and by several plants producing hemihydrate phosphogypsum [145, 146]. In the latter case, the free water associated with the use of the wet stacking method causes the hemihydrate material to convert to the dihydrate form (see Section 5.1.1.1). Although the conversion is not complete by the time the slurry reaches the stack, the management approach, in terms of the methods and equipment used, is the same as that for stacking phosphogypsum from dihydrate plants. Where water is available at a reasonable cost, wet stacking is easier, more reliable and less costly to carry out than dry stacking. It has a further economic benefit in that P₂O₅ recovery is improved if the water is recycled back to the process. Unlike dry stacking, wet stacking does not involve ‘construction around the clock’ and can be carried out with significantly less equipment and fewer personnel. Airborne dust generation, which can be a problem with dry stacking, is generally not a

problem with wet stacking because most of the surface area remains wet. Perimeter and internal partition dykes cover relatively limited and defined areas, and construction traffic is restricted to specific maintenance and access roads that are relatively easy to keep damp.

10.4.1. Wet stacking

In wet stacking operations (see Fig. 29), the phosphogypsum is mixed with water as it leaves the filtration system and is pumped as a slurry through a pipeline to a holding area within the stack where the solids settle out.

10.4.1.1. Water circuit

The water associated with wet stacking is managed either as a closed circuit (recirculating) system or an open circuit (once through) system:

- (a) In closed circuit systems, process water, also known as pond water, is used for transporting the phosphogypsum to the stack at a typical solids content of 20–30%. The water is clarified by allowing the solids to settle and is then decanted and pumped back to the plant, where it is reused for slurring the phosphogypsum or for other process applications. The recirculated process water becomes more acidic over time, usually reaching an equilibrium pH somewhere within the range 1–2, depending on process and climatic variables. The soluble P_2O_5 content of the acidic process water typically reaches 10 000–25 000 mg/L, but can be as high as 35 000 mg/L. Recirculated water can be used to wash the filters and re-slurry the gypsum cake to recover P_2O_5 . Washing with high P_2O_5 content water improves P_2O_5 recovery, which is one of the significant advantages of wet stacking. In a wet stack, the operator recovers soluble P_2O_5 from water entrained in the gypsum cake, with some additional P_2O_5 recovery from unreacted rock over time, as well as P_2O_5 contained in plant spills diverted to the pond. It is not uncommon to improve P_2O_5 recovery in a wet stack by as much as 3%. In wet climates, excess water due to rain may sometimes give rise to the need for additional treatment before discharging to a receiving water body.
- (b) In open circuit systems, the water used for generating the slurry, rather than being recirculated, is discharged as an effluent containing phosphates, fluorides and suspended solids. At coastal locations, the water may be extracted from the sea and discharged back to the sea after clarification. Seawater slurries are usually very dilute (about 5% solids by weight) and the pH of the water being discharged is greater than 2.

In the light of experience gained from the treatment of the highly acidic process water associated with closed circuit systems [147] and from dealing with spills in locations such as Florida and Louisiana, USA [33], it has been argued that the use of fresh water rather than recirculated water for creating the slurry would bring about significant environmental protection benefits, especially if the phosphogypsum is first washed with fresh water. Open circuit operation may also be favoured for other reasons; in arid climates, closed circuit operation may not be feasible because of evaporation from the pond, while in other situations, open circuit operation may be the more attractive option because of the existence of a large, nearby body of water, such as the sea. Nevertheless, closed circuit systems are generally preferred to open circuit systems because they do not generate liquid effluent.

Some phosphogypsum stacks have been converted from seawater (open circuit) systems to process water (closed circuit) systems. After conversion, the water returned to the plant from the stack is, initially at least, highly corrosive because of contamination with chlorides leached from the previously deposited phosphogypsum. Special measures would have been needed to reduce such contamination. The use of seawater at production facilities in Greece, Mexico, Spain and Tunisia has progressively stopped, although in most cases not as a result of decisions to convert to closed circuit systems but rather because of plant closure for financial reasons unrelated to the choice of water management system. In some cases, the change has been driven by the need to conform with environmental regulations, such as in Mexico and Tunisia, while in others the cost of changing process to achieve compliance has been so high that the production facility has simply closed altogether. In Spain, a change was made in the late 1990s from partial (20%) discharge to a closed circuit driven by the desire to eliminate completely any negative impact from process waters used for transporting phosphogypsum to the stacks.

10.4.1.2. Construction and operation of stacks

The stack perimeter is established by constructing ‘starter dykes’. Control of the slurry within the stack during operation is achieved using a technique known as elevated rim ditching, as illustrated in Fig. 32, and a system of pipes and valves, known as spigots, that direct the phosphogypsum slurry to various places on the top of the stack (see Fig. 33). The construction of starter dykes and rim ditches is usually carried out using earthmoving equipment, as shown in Figs 32 and 34. The use of wet gypsum for construction work avoids the generation of airborne dust. The emission of dust from maintenance and access roads as a result of their use by construction traffic is controlled by keeping the roads damp.



FIG. 32. Elevated rim ditching.



FIG. 33. Pipes and valves (spigots) for control of slurry on a stack.



FIG. 34. Stack construction work using wet phosphogypsum.

For safety reasons, rim ditches are constructed in accordance with specific geometric requirements and construction techniques, ensuring that all the rain that falls on the slurry ponds during operation is contained. A specified freeboard needs to be maintained to prevent the rim dams from being breeched by wave action in windy conditions. In Florida, USA, the freeboard requirement had to be increased following a succession of severe rainfall events which led to the near overflow of a stack at Piney Point in 2002 (see Fig. 35) [148].

A ditch or channel usually surrounds the stack to retain any lateral seepage at the toe of the stack and rainfall runoff contaminated by contact with non-vegetated side slopes. This ditch or channel may also serve as a process water cooling pond. A process water management system at a stack in Spain is shown in Fig. 36. In wet climates, excess water in the ditch or channel may be returned to the chemical plant as process make-up water or pumped to the top of the stack for storage, from where it is eventually consumed as process water or discharged to a receiving water body after appropriate treatment. The treatment of excess water usually consists of two-stage lime neutralization and clarification. The treated water contains high concentrations of dissolved solids, sulphate and sometimes ammonia. Process water that has not been in contact with phosphogypsum can,



FIG. 35. Pond near to overflow at Piney Point, Florida, USA, in 2002.



FIG. 36. Process water pond and perimeter channel at a phosphogypsum stack at Huelva, Spain.



FIG. 37. Vegetation of side slopes at a phosphogypsum stack at Huelva, Spain.

alternatively, be treated using reverse osmosis. The quantity of excess process water needing to be treated and discharged can usually be reduced, and possibly even eliminated, by having adequate surge capacity and by following appropriate procedures for the operation of the phosphogypsum stack and the chemical plant. For example, by conditioning and vegetating the bare stack slopes, as illustrated in Fig. 37, rainfall can, over time, be prevented from coming into contact with the phosphogypsum, thus avoiding contamination and enabling side slope runoff to be segregated and discharged without treatment.

10.4.1.3. Control of groundwater contamination

Contamination of groundwater by seepage from phosphogypsum stacks is an obvious environmental concern and it is common for new stacks to be constructed with an impervious bottom liner over a drain field that can be monitored for possible liner leakage. A typical stack liner is shown in Fig. 38. Measures for containing seepage from existing stacks can be implemented retrospectively. In some situations, a vertical hydraulic barrier comprising a soil–bentonite cut-off wall, or ‘slurry wall’, is built around the perimeter of the site, along with pressure relief wells. In other situations, a high density polyethylene (HDPE) geomembrane is installed on top of the stack, in order to serve as a bottom liner for subsequent deposits of wet phosphogypsum.



FIG. 38. Liner for a phosphogypsum stack.

In some regulatory jurisdictions, the use of a liner is a legal requirement. In Florida, USA, for instance, unless it had been demonstrated that groundwater impacts would be contained indefinitely within the property line or within a designated zone of discharge, all existing stacks and associated process water ponds had to undergo engineering modifications to contain any seepage or be closed and replaced by new lined facilities. Furthermore, all new stacks now have to include an impervious bottom composite liner system, consisting of an HDPE geomembrane 1.5 mm thick in combination with either a compacted clay layer beneath it or a compacted gypsum layer above it [149]. Nevertheless, it would appear that, depending on the conditions at the site, a liner is not always essential for controlling seepage. After many years of operation of stacks without liners, such as those at Huelva, Spain, it has been demonstrated that in many cases the substrate underlying the stack has remained impermeable and this, together with the inherent properties of phosphogypsum to form a largely impermeable compacted base, has resulted in there being little difference between lined and unlined stacks in terms of their potential for groundwater contamination. In Florida, USA, an evaluation of groundwater impacts from unlined stacks showed that heavy metals and radionuclides in the seepage water are attenuated by the



FIG. 39. A major sinkhole in an active phosphogypsum stack [33].

fine grained soils and calcareous strata upon which most of these structures are built [83, 150–152].

10.4.1.4. Control of fluoride emissions to the atmosphere

Fluorides, mainly in the form of hydrogen fluoride, are emitted from phosphogypsum pond water surfaces. These emissions can be reduced significantly if fluosilicic acid is extracted during the phosphoric acid production process.

10.4.1.5. Structural failures of stacks

Among the more spectacular problems associated with wet stacking is the occurrence of massive sinkholes, of which there have been four or five in Florida, USA, alone. Even a lined stack of modern design cannot cope with sinkholes of the size shown in Figs 39 and 40. Wet stacking of phosphogypsum is usually governed by regulations that typically require an extensive investigation of the subterranean conditions to determine the potential for sinkholes.

There have also been major spillages of acidic water due to structural failures of pond retention systems. While such failures are relatively rare, they



FIG. 40. A sinkhole in a phosphogypsum stack (helicopter gives a sense of scale) [33].

may have a significant impact on surface water bodies, more as a result of the acidic nature of the water than as a result of its radionuclide content [33].

Examples of events occurring in the USA involving failure or near failure are the following:

- (a) In 1997, tens of thousands of cubic metres of acidic water escaped from a stack in Florida and polluted a nearby river.²¹
- (b) In 2002, at a facility in Florida, a combination of extreme weather events and neglect caused by the bankruptcy of the owning company led to the near overflow of a stack, which would have resulted in total stack failure in a highly environmentally sensitive area. The only remedy was the emergency discharge of neutralized water by barge far out to sea, which was undertaken at very great cost.

²¹ State and local agencies are providing over \$1 million to restore, preserve and improve the estuarine habitats in the affected Alafia River and adjacent areas of Tampa Bay into which the river flows. The Alafia River Spill/Mulberry Phosphate Restoration Council that was formed to aid the river's environmental recovery announced that it would fund estuarine restoration projects to improve the habitat along the Alafia River (see, for example, <http://www.floridadep.com/southwest/news/101003.htm>).



FIG. 41. Side slope failure at Piney Point, Florida, USA, in 2003 (courtesy: Florida Department of Environmental Protection).

- (c) In 2004, 227 000 m³ of acidic water escaped from a stack, also in Florida, into a neighbouring creek. The apparent cause was damage done to the pond wall by waves driven by the force of a hurricane that hit the area.
- (d) In 2004, there was a spill from a stack in Florida, which fortunately did not extend beyond the property.
- (e) In 2005, about 65 000 m³ of acidic water escaped from a stack in Mississippi into surrounding marshland. The company argued that excessive rainfall was the cause, while state officials believed it was an error on the part of the company in trying to fill the process water pond too rapidly.

Other failures associated with stacks of modern design include side slope failure (see Fig. 41) and liner breaches, which by comparison are relatively inexpensive to deal with.



FIG. 42. Loading of phosphogypsum into trucks [146].

10.4.2. Dry stacking

In dry stacking operations, phosphogypsum leaving the filtration system is transported to the stack by belt conveyor or truck, without the addition of water (see Fig. 42). Upon reaching the stack, the material is deposited and spread using equipment such as mechanical stackers, movable belt conveyors and bulldozers (see Fig. 43). Dry stacking, although less widely practised than wet stacking, has been carried out in various parts of the world, including Brazil, Jordan, Senegal, Tunisia and several countries of the former Soviet Union. In Jordan, dry stacking is practised at Aqaba for dihydrate phosphogypsum and at Eshidiya for hemihydrate phosphogypsum.

The moisture content of the phosphogypsum emerging from the filtration system is sufficient to prevent the emission of airborne dust from the material while it is being transported on belt conveyors or in trucks. However, the spillage of phosphogypsum from conveyor belts and trucks, as well as at any transfer points, is a potential source of airborne dust if the spilt material is allowed to dry before being removed. For this reason, the conveyor may need to be enclosed. The use of a high pressure water spray on the underside of the conveyor at the discharge end removes any phosphogypsum adhering to the belt. The wash water from the spray system is collected and consumed as process water or appropriately treated and discharged.



FIG. 43. Spreading of phosphogypsum in a dry stacking operation.

When dry stacking operations are carried out in areas with unusually high rainfall, such as at Santos, Brazil, where the average annual rainfall is 3 m, the stack surfaces remain permanently damp and no significant emissions of airborne dust occur. In less extreme climatic conditions, the stack surfaces dry out between periods of rainfall. A thin, fragile crust forms on the stack surface, which can help to minimize the emission of airborne dust as long as it remains undisturbed by the wind and by the construction equipment used for placing and spreading the phosphogypsum. The emission of airborne dust as a result of the disturbance of this crust creates not only a dust problem, but also leads to the emission of fluorides and radon that emanate from the surfaces of the dust particles. Dust emission from dry stacking operations (and the resulting fluoride and radon emissions) is controlled by limiting the extent of the active placement area and haul roads and by spraying the surfaces with water to keep them damp.

Rainfall runoff from the stack is collected and returned to the chemical process or used to suppress the emission of airborne dust from maintenance and access roads. Dry stacking does not eliminate the possibility of acidic seepage from the base of the stack and from the toe of the side slope. Even in desert climates, a bottom liner may need to be incorporated to prevent groundwater contamination because vertical cracks tend to form within the stack as a result of differential settlement and/or side slope instability. These cracks create paths for the entry of water deep into the stack during relatively rare heavy rainfall events. Filling of these cracks with phosphogypsum minimizes the entry of rainwater and

also helps prevent possible slope instability caused by hydraulic pressures generated within the water filled cracks.

10.4.3. Environmental impacts

As explained in Sections 10.4.1 and 10.4.2, measures are taken during the construction and operation of phosphogypsum stacks to ensure that the runoff of contaminated rainwater is contained within the stack perimeter, that effluent water is treated before discharge and that seepage into the groundwater and emission of dust to the atmosphere are controlled. These measures are designed to keep the environmental impacts of phosphogypsum stacks within acceptable bounds. Contamination of groundwater near phosphogypsum stacks is, in any case, restricted by the limited solubility of radium and other radioactive species in sulphate form [81]. A detailed investigation was carried out on the processes responsible for controlling the interaction and release of radionuclides from phosphogypsum from a phosphogypsum stack at Piney Point Phosphates in Florida [81]. On the basis of measurements of activity concentrations in groundwater collected from several monitoring wells around the stack, it was concluded that various removal mechanisms, including adsorption within the stack, precipitation within the soil horizons just below the stack and interception of stack fluids by drainage ditches, prevent large scale migration of radionuclides to the underlying aquifer. However, some of the laboratory studies on the leaching characteristics of ^{226}Ra from phosphogypsum showed a dependence on various conditions such as solution:solid ratios, contact times and acidity on dissolution rates [153, 154]. Forced leaching experiments indicated that uranium dissolution largely depends on the presence of phosphoric acid traces in phosphogypsum. Studies indicated that the leaching of radium may be slow in field conditions near phosphogypsum stacks, especially when the phosphogypsum is previously washed and stored.

An investigation of the impact of phosphogypsum stacks on surface water systems was carried out in the Cubatão region of southern Brazil [155]. Sediments were sampled from a river receiving effluent discharged from nearby phosphogypsum stacks. Near the point of discharge, the concentrations of barium, zirconium and thorium in the sediment were found to be elevated above local background levels. The samples also showed the presence of rare earth elements at elevated concentrations and with a higher degree of fractionation in comparison with the concentration ratios of individual rare earth elements in phosphate rock. The mean concentrations of cerium in surface and core sediments were 151 and 387 ppm, respectively, which may not be desirable in surface water streams. These results were consistent with the contaminants having originated from the phosphogypsum, the characteristics of which reflected

the composition of the Catalão igneous phosphate ore, with some modification as a result of the phosphoric acid production process. The sediment contamination levels were found to decrease rapidly in the downstream direction, indicating that the influence of the phosphogypsum stacks was confined to a small area.

The emission of fluorides from ponds in wet stacking operations has been measured. The rate of emission was found to be in the range $0.01\text{--}0.10\text{ kg}\cdot\text{ha}^{-1}\cdot\text{d}^{-1}$. Elevated levels of fluorides have been found in vegetation growing very close to a phosphogypsum stack [156]. The repeated ingestion of such vegetation by cattle over periods of years may cause fluorine toxicosis, also known as fluorosis or brittle bone syndrome.

In some countries, the recent spread of residential and commercial property development has resulted in members of the public living and working ever closer to phosphogypsum stacks. Some older stacks have now become surrounded by developed metropolitan areas. In Huelva, Spain, for instance, residential apartments are being built less than 300 m from an operating stack. Nevertheless, measurements have indicated that exposure levels diminish very rapidly with distance from the stack [94].

Measurements of radon concentrations in the air around phosphogypsum stacks have been reported from a few countries. The average radon concentration above a phosphogypsum stack in Huelva was recorded as 13.1 Bq/m^3 over a measurement period of six months and comparable with the natural background levels measured in the adjacent residential areas [157]. Measurements were also reported from a phosphogypsum stack in India [74]. The ^{222}Rn concentrations were $9\text{--}45\text{ Bq/m}^3$ in the indoor environment, close to the stack, and were also comparable with the background concentrations in the local environment.

The radon emanation factor for phosphogypsum is typically about 0.2 [158]. Measurements of the emission of radon have been made on the surfaces of several phosphogypsum stacks in central Florida, USA [150, 151], and on one stack in south-western Spain [159]. The results are shown in Table 33. The Spanish study found that radon exhalation rates above the surface of a stack were an order of magnitude higher than those found in the reference site (agricultural soil), with no significant enhancement in radon exhalation rates during tillage or digging of the stack surface. However, since the stack surface is open to the atmosphere, no significant buildup of radon above the stack was observed.

Investigations have also been carried out at Huelva, Spain, on the aerosol activity concentrations above phosphogypsum stacks after preliminary restoration work [160]. The ^{238}U , ^{226}Ra and ^{210}Pb concentrations in airborne dust were 0.016 , 0.01 and 0.6 mBq/m^3 , respectively, and were comparable to background levels. The corresponding incremental inhalation dose received by maintenance workers was estimated to be $0.7\text{ }\mu\text{Sv/a}$. The formation of a hard crust on the surface of inactive stacks also prevents resuspension of particles and

TABLE 33. RADON EMISSION FROM PHOSPHOGYPSUM STACKS

Location	Mean Ra-226 concentration in phosphogypsum (Bq/g)	Mean radon flux (Bq·m ⁻² ·s ⁻¹)	Radon flux per unit Ra-226 concentration (Bq·m ⁻² ·s ⁻¹ per Bq/g)
<i>Central Florida, USA [150, 151]:</i>			
Stack, side slopes, access roads ^a	1	1	1
Intermittently ponded areas	1	0.075	0.075
<i>South-western Spain [159]:</i>			
Undisturbed surface	0.73	0.01–0.16	0.014–0.22
Surface disturbed by tilling	0.73	0.04–0.3	0.055–0.41
Agricultural soil (for comparison)	0.035	0.003–0.011	0.086–0.31

^a The individual mean radon fluxes from the stack, side slopes and access roads were similar.

these results indicate that dust inhalation on a restored phosphogypsum stack does not result in significant exposure.

Several studies have been performed to determine the dose received by workers engaged in phosphogypsum stacking operations. The gamma doses received by maintenance workers on stacks in Spain were 0.25–0.35 mSv/a, assuming 2000 h of occupancy, which is quite conservative [157]. In this context, it is worth mentioning that workers perform a variable but significant fraction of their work inside trucks and other machinery which act as shielding against gamma radiation, implying even lower doses in practice.

10.5. USE OF PHOSPHOGYPSUM

10.5.1. Agriculture

Phosphogypsum is used in agriculture throughout the world [33], for example in Australia, Bangladesh, Brazil, Egypt, India, Kazakhstan [136], Pakistan, Spain [161], the Syrian Arab Republic and the USA [162]. In Brazil, 40% of all phosphogypsum produced is used in agricultural applications. In California, USA, a stack of phosphogypsum originating from phosphate rock from Idaho and Wyoming was utilized completely for agricultural purposes, prior to such use being restricted by regulations in 1989. A very small quantity of phosphogypsum with a low radium content produced in Florida, USA (representing only 0.03% of total



FIG. 44. Soil near Huelva, Spain, prior to remediation with phosphogypsum (courtesy: University of Seville, Spain).

Florida production), continues to be used as a soil amendment in peanut farming. In the European Union, phosphogypsum is permitted for use as a soil amendment under the category ‘calcium sulphate’ [163, 164]. Phosphogypsum contributes to agricultural production in four principal ways:

- (i) Reclamation of land such as estuarine marsh in order to render it agriculturally productive;
- (ii) Remediation of saline and sodic soils (see Fig. 44);
- (iii) Amendment of soil to prevent crusting and to enhance water retention;
- (iv) Fertilization of soil for growing crops and pasture.

Phosphogypsum usually does not need to be tilled into the soil. Freshly generated phosphogypsum is unweathered and moist, and in this state it can be applied directly to the surface of the soil using conventional methods of distribution (see Fig. 45).

A large area of land near Huelva, Spain, has been progressively reclaimed by the application of phosphogypsum and returned to productive agricultural use. An aerial view of the reclaimed land is shown in Fig. 46. This site is particularly



FIG. 45. Direct application of phosphogypsum to soil (courtesy: University of Seville, Spain).



FIG. 46. Land reclaimed by the use of phosphogypsum (courtesy: University of Seville, Spain).

significant in terms of risk assessment since it is the only documented area in the world which can be used to study the impact of 40 years of continuous use of phosphogypsum on soils, a practice that still continues at this locality.

The benefits of applying phosphogypsum to saline and sodic soils are described in Refs [136, 161, 162] and include:

- (a) Reduced sodium and aluminium toxicity of the soil;
- (b) Increased calcium and sulphur dissolved from the phosphogypsum;
- (c) Increased ammonia retention by the soil;
- (d) Increased water retention of the soil through better conditioning;
- (e) Greater water efficiency.

The use of phosphogypsum as a fertilizer, typically at application rates of 100–600 kg/ha, has been found to increase significantly the production rates of the following crops [33]:

Alfalfa	Carrots	Lemons	Peaches	Sugar beet
Apples	Citrus	Lentil	Peanuts	Sugar cane
Avocado	Coffee	Limes	Pepper	Sweet sorghum
Bahia grass	Corn	Lucerne	Pineapple	Tea
Barley	Cotton	Maize	Rapeseed	Tobacco
Beans	Cover crops	Mustard	Rice	Tomato
Beets	Forage	Niger	Rye grass	Turnip
Bermuda grass	Frasier fir	Onion	Sorghum	Upland rice
Black gram	Groundnuts	Oranges	Soya beans	Vegetables
Cabbage	Guinea grass	Pasture grass	Squash	Wheat

Phosphogypsum is often used in its unmodified state. Depending on the specific crop application, however, it may be necessary to remove the acidic water (and even some of the other impurities) contained within it. For example, phosphogypsum ‘harvested’ for agricultural use from the inactive portion of a stack in northern Florida, USA, is first exposed to rainwater for about a year. When the rainwater permeates the phosphogypsum, the acidic process water contained in the phosphogypsum is displaced, causing the pH of the harvested phosphogypsum to increase to a value greater than 5. In general, any removal of impurities has to be kept to a minimum to avoid making the use of phosphogypsum uneconomic compared with the use of relatively inexpensive natural gypsum.

The use of phosphogypsum as a soil amendment has been studied extensively to determine the extent to which the introduction of additional heavy metals and radionuclides through the application of the phosphogypsum could lead to possible human health effects via the following pathways:

- (a) Uptake of radioactivity and heavy metals from the amended soil by edible crops;
- (b) Inhalation of radionuclides in airborne dust during the application of the phosphogypsum;
- (c) External exposure rates due to the amended soil;
- (d) Groundwater contamination;
- (e) Radon emission from the amended soil.

In an evaluation of the application of phosphogypsum as a soil amendment and fertilizer [165], phosphogypsum with a ^{226}Ra activity concentration of about 1 Bq/g was assumed to have been applied to the soil every second year for 100 years after an initial application of twice the biennial application rate. Six scenarios were considered, involving various rates of phosphogypsum application in the range 1.66–10 t/ha and tillage depths of 22–46 cm. After the 100 year period, ^{226}Ra concentrations in the soil were calculated to be 0.03–0.12 Bq/g.

An investigation was carried out to determine the effect of phosphogypsum, when used as a calcium fertilizer for the production of crops such as cotton, on the resulting levels and behaviour of radionuclides [166]. Phosphogypsum with a ^{226}Ra activity concentration of 0.51 Bq/g was applied at rates of 13 and 26 t/ha in conjunction with manure at a rate of 30 t/ha. The concentrations of ^{226}Ra in the water draining from the fertilized areas were similar to those reported for non-treated areas (2.6–7.2 mBq/L).²² The results revealed that the activity concentrations of ^{226}Ra in the crops were not affected by the phosphogypsum treatment and that there was no accumulation of radioactivity in the soil. Similar studies to investigate the buildup of radioactivity in soil or uptake by crops show no significant uptake in most cases [167, 168]. In a study carried out in five land parcels of the central Florida phosphate district, approximately 70 individual

²² While the ^{226}Ra concentrations in the drainage water were not found to be elevated, the concentration of ^{238}U was found to be 200 mBq/L; an order of magnitude higher than normal. However, the ^{234}U : ^{238}U isotopic ratio in the uranium-enriched drainage water was 1.16, as opposed to a ratio of 1 in the phosphogypsum and other phosphorus fertilizers used, from which it was concluded that most of the additional uranium in the drainage water did not originate from the phosphogypsum but was thought to originate instead from the uranium naturally present in the soil (at a ^{238}U activity concentration of 0.025 Bq/g) that had become desorbed.



FIG. 47. Greenhouse studies involving various crops (courtesy: University of Seville, Spain) [170].

food samples were collected and analysed for ^{226}Ra , ^{210}Pb and ^{210}Po [62, 63]. Concentrations of ^{226}Ra and ^{210}Pb in food grown on mined phosphate lands were statistically higher than the concentrations of these nuclides in foods from unmined lands. However, an upper estimate of the likely incremental increase in annual ingestion dose was only 0.027 mSv. A radiological impact assessment of the application of phosphogypsum in agriculture was reported from Greece [169]. The concentration of ^{226}Ra in rice and other agricultural products produced from soil tilled with phosphogypsum ranged from 0.0004 to 0.002 Bq/g and the estimated ingestion dose was 0.86 $\mu\text{Sv/a}$.

A completely randomized greenhouse experiment was carried out in Spain growing tomato (*Lycopersicum esculentum* Mill L.) using a reclaimed marsh soil amended with various rates of phosphogypsum up to 20 t/ha to investigate the transfer of ^{238}U , ^{226}Ra , ^{210}Po , Pb and Cd to the crop [170]. The experimental set-up is shown in Fig. 47. The concentrations of ^{238}U and ^{226}Ra in the crops were below the detection limit in all cases and the concentration of ^{210}Po was 0.0004–0.0007 Bq/g on a dry weight basis. The results also showed that the

application of phosphogypsum as a calcium amendment for agricultural purposes could lead to some uptake of cadmium in the plants.

In the Cerrado region of Brazil, where significant amounts of phosphogypsum are used for agricultural purposes, a field study explored the impact on two typical soils of the region, one clayey and the other sandy. These analyses included an evaluation of the mineralogical composition, the organic matter content and the concentrations of P, K, Ca, Mg and Al. The concentrations of radionuclides and metals in the phosphogypsum and soil samples were also measured. The organic matter content of the soil samples was low and the potential acidity high. The mean ^{226}Ra activity concentration in the phosphogypsum samples was 0.252 Bq/g. In addition, this study verified that the concentrations of radionuclides and metals in the phosphogypsum were lower than the background concentration in the clayey oxisol soils of Sete Lagoas, Minas Gerais, Brazil. These results indicated that the application of phosphogypsum as a soil amendment in agriculture would not have a significant impact on the environment [171].

A three year field study in Florida, USA, involving the application of phosphogypsum at relatively low rates (up to 4 t/ha), showed no statistically significant increases in radionuclide concentrations in soils and groundwater or in the levels of airborne radon and gamma radiation measured 1 m above the plots [172]. A subsequent study, which has become a benchmark because of its comprehensive methodology and scope [173], developed data to assist in the assessment of the environmental impacts of the application of phosphogypsum at higher rates (up to 20 t/ha) to an established bahia grass pasture, primarily in terms of the radionuclides in phosphogypsum and secondarily in terms of the heavy metal impurities. The results can be summarized as follows:

- (a) Exposure from the inhalation of radon progeny was determined from measurements of the ^{226}Ra activity concentration in the soil, the radon flux from the soil and the radon concentrations in the air. For the application of phosphogypsum at a rate of 0.4 t/ha over a 100 year period, the incremental radon flux from the amended soil was projected to be about 40% of the mean value for undisturbed land (with no phosphate mineralization) in the region. For a house constructed on the amended soil, the phosphogypsum in the soil was estimated to increase the indoor radon concentration by about 1–10 Bq/m³ (representing, for a typical house, an increase of about 2–20%). For a cumulative treatment of up to 40 t/ha, the phosphogypsum was predicted to contribute less than 3.7 Bq/m³ to the radon concentration over the field.
- (b) Exposure to external gamma radiation was determined from dose rate measurements made following a single treatment of phosphogypsum of up

to 40 t/ha. After the first year, no gamma exposure attributable to the phosphogypsum could be detected. It was concluded that the radionuclides from the phosphogypsum had penetrated the soil or had been removed by weathering or harvesting. The incremental annual effective dose received by an individual remaining permanently on the treated land was projected to be 0.028 mSv after 100 years.

- (c) Exposure from the ingestion of radionuclides in water and food was determined from measurements of the activity concentrations of ^{226}Ra , ^{210}Pb and ^{210}Po in samples of soil, water and forage. The results suggested that the radionuclides contained in the phosphogypsum had limited mobility in surface water and groundwater during the first two years after application to the soil. However, it is possible that they may have been gradually mobilized, appearing in the groundwater at a later date. The activity concentrations of ^{226}Ra in shallow groundwater after 100 years of phosphogypsum use were projected to be about 0.1 Bq/L. Levels of ^{210}Pb were projected to be similar to the baseline levels in runoff and shallow groundwater (<0.04 Bq/L). Doses to humans from the ingestion of animal products that had been contaminated with radionuclides taken up by forage appeared to be within the range of variation in a normal diet.

10.5.2. Construction of buildings

Phosphogypsum has been used as a raw material for cement [174, 175] and as a source of plasterboard. Other construction uses include the production of bricks [176], blocks [177], tiles, artificial stone and even boats [178]. Countries using phosphogypsum for building purposes, usually with certain restrictions, include Belgium, Brazil and India. Phosphogypsum is viewed as a potential building material in South Africa, where the construction of low cost housing is being encouraged. Almost all the uses of phosphogypsum for building products require the phosphogypsum to be well washed to remove the acidity from its residual water content and in some cases further processed to remove residual phosphate.

Recent developments in the phosphate industry in countries with rapidly expanding economies, such as China, have led to a major increase in the production of phosphogypsum, which in turn has stimulated interest in its use, including its use in construction applications [179–182]. As a result, the relevant authorities have taken a greater interest in establishing the necessary conditions for the safe use of phosphogypsum [183, 184]. Exposure to building materials incorporating phosphogypsum has been comprehensively and continuously studied [185, 186]. Exposure levels have been found to depend strongly on exactly how the phosphogypsum is used — exposure from phosphogypsum

panels, for instance, depends on parameters such as panel design, thickness and density. While most studies show that exposure levels are not likely to be of serious concern, experience suggests that the use of phosphogypsum in building materials is not being given the attention that it perhaps deserves. Attention is often diverted too readily to other, more widely established uses of phosphogypsum such as agricultural applications. This situation appears to have been brought about by two factors in particular:

- (i) Compliance with local legal criteria is often raised as an obstacle, often leading to potential uses of phosphogypsum in building materials being dismissed without consideration of the possibility that the criteria themselves might be inappropriate. Ideally, the establishment of criteria for the use of phosphogypsum would be based on empirical scientific evidence relevant to the local situation and would take account of prevailing economic and social factors. Not surprisingly, perhaps, the criteria tend to be based, instead, on a more simplistic approach using theoretical modelling, which is likely to be generic, conservative and limited to purely radiological considerations. Consequently, the criteria end up being unnecessarily restrictive.
- (ii) All too often, the use of phosphogypsum is considered only on its direct technical and economic merits as a substitute for other building materials such as natural gypsum (which, in many countries, is in good supply at a competitive price). The broader, less direct benefits of using phosphogypsum in building materials, particularly the additional opportunity that it offers for reducing the financial and environmental liabilities associated with the indefinite storage of phosphogypsum, are not taken into consideration.

Phosphogypsum has also been used in some countries in civil construction applications other than buildings and roads. For instance, the phosphogypsum produced by the largest wet process phosphoric acid plant in China has been used for civil engineering projects such as the construction of the Three Gorges Dam [33], which accounts for nearly 80% of the annual production from the plant.

10.5.2.1. Phosphogypsum in cement

The use of phosphogypsum in cement and related products such as plaster provides an opportunity for consuming large volumes of material. Various options have been pursued in several countries [187–189]. In Europe, the use of phosphogypsum in this manner was well established from the 1960s onwards. In

former phosphogypsum producing countries such as Belgium and France, the opportunities for significant commercial benefit from the use of phosphogypsum in cement and plaster led to investigations being focused on these applications rather than on other construction applications such as road construction [190].

In Spain, activity concentration measurements were made on two types of cement containing phosphogypsum [185]. The results of the measurements are given in Table 34 — the phosphogypsum used in this application is identified as PG-1 and PG-2. The activity concentrations of ^{226}Ra , ^{210}Pb and ^{210}Po in the cement were much lower than those in the phosphogypsum. The activity concentrations of ^{40}K were higher, while the activity concentrations of ^{232}Th were similar. The significant dilution of activity content indicates the potential for use of phosphogypsum in building materials. Detailed information based on dose assessments can be used to determine further the applications of phosphogypsum as an additive to cement for building applications on a case-by-case basis.

10.5.2.2. Phosphogypsum panels

In a study conducted in Brazil [191–193], exposure levels were measured inside an experimental house constructed using relatively thin, high strength phosphogypsum panels. The walls were composed of double sets of joined panels with a thickness of 1.5 cm and a 15 cm gap between two such joined panels. For ceiling panels the thickness was 1 cm. The house is shown in Fig. 48. The mean radionuclide activity concentrations in the phosphogypsum panel material from three production locations were 0.02–0.39 Bq/g for ^{226}Ra , 0.03–0.85 Bq/g for ^{210}Pb , 0.03–0.25 Bq/g for ^{232}Th and <0.08 Bq/g for ^{40}K . For various realistic scenarios involving the exposure of a house occupant, the projected average incremental dose was found to be 0.02–0.20 mSv/a, with the range of values

TABLE 34. ACTIVITY CONCENTRATIONS IN PHOSPHOGYPSUM AND IN CEMENT CONTAINING PHOSPHOGYPSUM

Material	Activity concentration (Bq/g)				
	Ra-226 ^a	Pb-210	Po-210	Th-232 ^a	K-40
Phosphogypsum PG-1	0.205	0.161	0.214	0.019	—
Phosphogypsum PG-2	0.170	0.165	0.174	0.006	0.013
Cement 1	0.027	<0.056 ^b	0.021	0.017	0.730
Cement 2	0.027	<0.036 ^b	0.025	0.013	0.613

^a The activity concentrations of Ra-226 and Th-232 were determined by equating them to the measured values of Bi-214 and Ac-228, respectively.

^b Detection limit.



FIG. 48. An experimental house constructed using phosphogypsum.

reflecting the different origins of the phosphogypsum. The radon concentrations measured in the experimental house were found to be 45–119 Bq/m³, averaged over a period of 15 months, changing detectors every three months. No information on the ventilation conditions in the experimental house was available. However, on the basis of the available data, radon could possibly be an exposure pathway in buildings constructed using phosphogypsum with high radium concentrations.

The use of phosphogypsum plasterboard panels in house construction has also been studied in Australia [194, 195]. The annual effective dose received by the occupant of a room of dimensions 5 m × 5 m × 3 m was calculated, assuming that the walls and ceiling were lined with 1 cm thick phosphogypsum panels having a ²²⁶Ra activity concentration of 0.4 Bq/g. The annual effective dose attributable to the phosphogypsum was 0.13 mSv, representing an increment over that for normal construction of 14%. On the basis of measurements made on the panels to determine their ²²⁶Ra content and ²²²Rn exhalation rate, exposure to radon progeny was calculated by modelling a typical building configuration. The measured ²²²Rn exhalation rates in the untreated plasterboard were in the range 0.0005–0.001 Bq·m⁻²·s⁻¹. For air exchange rates greater than 0.5 and up to 5 air changes per hour, the incremental annual effective dose from radon progeny

inhalation was found to be between 0.02 and 0.16 mSv for the maximum measured radon exhalation rate. It was also found that the radon exposure was reduced if the surfaces of the panels were coated with paint or cardboard. Exposure was also reduced by 15–20% if the very fine particles were removed from the phosphogypsum prior to manufacture of the plasterboard. The annual effective dose received via the inhalation of airborne dust by a worker installing the plasterboard was also determined, based on certain assumptions. For particles with an AMAD of 5 μm and having an initial source concentration of 0.4 Bq/g ^{238}U and progeny in equilibrium and a dust concentration of 1 mg/m^3 , the inhalation dose was estimated to be 0.05 mSv for an exposure period of 2000 h.

The use of phosphogypsum in building and construction materials has also been investigated in India [196]. Measurements carried out inside a plasterboard plant showed absorbed dose rates in the range 0.03–0.04 $\mu\text{Gy}/\text{h}$ in the phosphogypsum mixer, aligner, tensioner and hammer mill areas. Higher absorbed dose rates up to 0.1 $\mu\text{Gy}/\text{h}$ were measured in the product storage area. The mean radionuclide activity concentrations in the 1.25 cm thick plasterboard sheet were 0.09 Bq/g for ^{226}Ra , 0.009 Bq/g for ^{238}U , 0.005 Bq/g for ^{232}Th and 0.015 Bq/g for ^{40}K . Various exposure scenarios were postulated and a dose estimation for each of these scenarios was carried out using methodologies reported elsewhere for the assessment of radiation exposures from building materials containing radionuclides. The maximum doses estimated for the use of phosphogypsum panels in ceilings, walls and floors were in the range 0.15–0.46 mSv/a. Exposure to radon exhaled from the material was not considered, as it was not a significant exposure pathway under the prevailing ventilation conditions. In formulating a regulatory guideline, glass fibre reinforced phosphogypsum panels having dimensions of 12 m \times 3 m \times 1.25 cm with 48 hollow cavities were evaluated for likely exposures and indicated doses as high as 4.5 mSv/a. However, by restricting the ^{226}Ra concentration in the phosphogypsum to below 1 Bq/g and by applying a surface activity concentration limit of 40 kBq/m^2 , the dose could be limited to 0.3 mSv/a. The regulatory guidance also suggested mixing with other ingredients such that the ^{226}Ra concentration in the bulk material is less than 1 Bq/g.

10.5.2.3. Phosphogypsum in glass and glass ceramics

Glass and glass ceramics can be readily manufactured from phosphogypsum and tailings sand [197–201]. Since the materials are vitrified, they exhibit low radon emanation fractions. Products include:

- (a) Glass ceramic floor, wall and roof tiles;
- (b) Synthetic wollastonite (CaSiO_3) fibres used in ceramics and paints and as a non-toxic substitute for asbestos;

- (c) Synthetic stone for building facades;
- (d) Abrasives;
- (e) Flat 'privacy' glass;
- (f) Container glass for selected beverages and agricultural products.

An assessment of doses received by a house occupant as a result of gamma radiation from the use of phosphogypsum in tiles is reported in Ref. [197]. In a typical exposure scenario, the tiles were assumed to be used on the floors of the kitchen, bathroom and entrance hall and on the walls of the bathroom, with the following dimensions:

- (a) Tile thickness: 7.6 mm.
- (b) Kitchen floor: 5 m × 5 m.
- (c) Bathroom and entrance hall floors: 3 m × 3 m.
- (d) Bathroom walls: 2 m × 3 m.

The distance from the source was assumed to be 1 m for floor tiles (or 0.2 m for a child) and 0.5 m for wall tiles. The results of the dose assessment for this typical exposure scenario are given in Table 35. Results for what is considered to be an extreme exposure scenario, involving a longer annual exposure period associated with a single 10 m × 10 m room having 7.6 mm thick floor tiles and 10 mm thick roof tiles (unshielded), are also given in Table 35. The most exposed adult is estimated to receive an annual dose of 0.06 mSv (or 0.29 mSv for the extreme scenario), while the most exposed child receives 0.09 mSv (or 0.46 mSv for the extreme scenario).

The use of phosphogypsum glass ceramic tiles in a house has also been investigated in a modelling study with respect to exposure to radon [197]. The material was assumed to consist of CaO and SiO₂ at a mass ratio of 1:3 and to have a ²²⁶Ra activity concentration of 0.88 Bq/g, a density of 2600 kg/m³ and radon emanation of 0.00021 Bq·m⁻²·s⁻¹. The analysis showed that for a house tiled completely with phosphogypsum tiles, the radon exhalation rate was only 10% of that for normal construction materials.

10.5.3. Construction of roads

One of the more widely studied and tested uses of phosphogypsum in construction is for road building [130, 132, 202]. Unpaved phosphogypsum roads are commonplace at phosphoric acid production facilities, especially on and around phosphogypsum stacks. Initial work on the use of phosphogypsum for the construction of paved roads in Belgium [203, 204] and France [205–208] in the 1970s and 1980s focused on its use in embankments [209, 210] and for road

TABLE 35. EXPOSURE TO CERAMIC TILES MADE WITH PHOSPHOGYPSUM [197]

Location	Absorbed dose rate ($\mu\text{Sv/h}$)		Annual occupancy period (h)		Annual effective dose (mSv)	
	Adult	Child	Adult	Child	Adult	Child
<i>Typical exposure scenario:</i>						
Kitchen	0.025	0.058	2000	1200	0.05	0.07
Entrance hall	0.016	0.048	65	65	<0.01	<0.01
Bathroom, floor	0.016	0.048	250	250	0.004	0.012
Bathroom, walls	0.024	0.024	250	250	0.006	0.006
Total					0.06	0.09
<i>Extreme exposure scenario:</i>						
Floor	0.040	0.070	4500	5250	0.18	0.37
Roof	0.024	0.017	4500	5250	0.11	0.09
Total					0.29	0.46

stabilization [211]. These efforts came to an end for commercial reasons whereby the phosphogypsum under investigation had a more valuable market outlet in wall boards for buildings than in road construction. While some investigative work on the use of phosphogypsum in embankments continued elsewhere [212], ongoing work became focused on the road bed, where phosphogypsum mixed with 5–7% cement and, in some cases, fly ash emerged as the best option [132]. The construction of pilot roads built in this manner has been successfully carried out in climatic regions with wet–dry cycles, such as in Florida, USA [186, 213], South Africa [214] and in climatic regions with freeze–thaw cycles such as in Finland [215]. Although no further paved roads have been built, research into the optimization of the use of phosphogypsum in road construction has continued [216, 217].

It has been determined that the use of phosphogypsum in road base applications could consume 25 000 t per lane kilometre, which would translate into an annual phosphogypsum consumption of some 140 million t in the USA alone. It has also been determined from the pilot studies carried out that the use of phosphogypsum as a road bed material is no more expensive than the use of more

traditional materials and may actually be less expensive when the full life cycle cost is considered [214]. In Florida, USA, in areas near large quantities of readily available phosphogypsum, the construction cost was found to be close to one third of the cost of using conventional material. With regard to resource conservation and recycling, the pilot studies indicate a potential virgin resource saving of up to two thirds [215]. The major constraints on the use of phosphogypsum in road construction are economic, cultural and regulatory:

- (a) Economic constraints [218]: Owing to transport costs, any bulk material used for road construction needs to be readily available from a source located reasonably near the construction site. For phosphogypsum to be viable as a road construction material, it has been estimated that its source would have to be located no more than 150–200 km from the construction site [219].
- (b) Cultural constraints: Road builders seem reluctant to substitute phosphogypsum for conventional road bed materials. To overcome such reluctance, a shift in attitudes towards the use of phosphogypsum would be necessary [132]. It has been suggested that the offer of some initial incentive would eventually change current perceptions concerning the use of phosphogypsum, similar to the way in which perceptions in the cement industry have changed from considering fly ash as a waste to considering it as a valuable resource [132].
- (c) Regulatory constraints: Even where the environmental impact is considered acceptable once the road is built, other regulatory constraints may still exist. In the USA, for instance, the use of phosphogypsum for road construction is, in effect, prohibited because authorization cannot be obtained for the transport of the material to the construction site [220].

10.5.3.1. Technical considerations

Phosphogypsum has successfully been used as a binder for base course mixtures. Phosphogypsum based mixtures are more workable than clay based mixtures. Delays due to rain during construction are reduced because the compacted mixture does not absorb significant amounts of water. Shrinkage cracks and swelling, which often negatively affect the performance of clay based road beds, are greatly reduced. The stability of compacted phosphogypsum mixtures is superior to that of clay mixtures [186] and there is evidence that the use of phosphogypsum, if correctly optimized, leads to a progressive strengthening of the road bed over time [214, 215].

In Texas, USA, road bases for city streets, shopping centres, truck terminals, parking lots and loading platforms were successfully constructed using

cement and fly ash stabilized phosphogypsum and fluorogypsum²³ [221, 222]. This was followed, in 1988–1991, by the construction of several experimental sections of road directed towards establishing materials selection criteria, a suitable mix design rationale and construction procedures to permit stabilized phosphogypsum road bases to be used in Texas [223]. The concepts generated were successfully demonstrated in 1991 when a two lane 100 m test section was constructed using a road base consisting of a 7% cement stabilized phosphogypsum mixture with an unconfined seven day compression strength of 3.1 MPa. A second experimental test section was constructed in 1992 using a road base containing equal proportions of bottom ash (comprising three parts boiler slag to one part cinder ash) and phosphogypsum. Two additional road sections were built in 1993 using phosphogypsum blended with fly ash and cement–fly ash, respectively [132]. After two years, these sections were found to be performing well.

In Florida, USA, two experimental roads were built in 1986–1987 using both dihydrate and hemihydrate forms of phosphogypsum [224, 225]. The results of the evaluations are reported in Refs [226–228]. It was concluded that phosphogypsum, when subjected to optimum mixing and compaction, could be transformed into a solid of high strength that is effective as a binder to stabilize on-site soil. Phosphogypsum and sand mixtures, stabilized with a small amount of cement, possessed a load bearing capacity higher than that of locally mined limestone, which was at that time the material of choice for road bases in the region. It was also demonstrated that the incorporation of phosphogypsum into a cement based mixture for making ‘roller compacted concrete’ (a form of concrete widely used for road construction) led to improved compaction and strength properties [229]. The road bed described in Ref. [224] is shown in Fig. 49, which shows the condition after 25 years of use. The picture was taken during routine resurfacing. While the phosphogypsum is clearly not mixed in fully with other road bed materials, it has, nevertheless, lost none of its load bearing strength. As a result, the only maintenance requirement was a new layer of asphalt.

10.5.3.2. Environmental impact

The dissolution and/or leaching of the road bed mix, especially the phosphogypsum component, and any volume change due to changes in water content and/or chemical reactions were evaluated in terms of their potential environmental impact [228]. Laboratory tests showed that leaching from cement

²³ Fluorogypsum is a residue from the production of hydrofluoric acid.



FIG. 49. Experimental road bed in Florida, USA, incorporating phosphogypsum (courtesy: Florida Industrial and Phosphate Research Institute).

stabilized phosphogypsum was below levels of concern, even in the TCLP²⁴ test designed to simulate the leaching of toxic elements such as mercury and cadmium from material disposed of in a landfill facility. It was found that the leaching of heavy metals into the environment from the phosphogypsum component was lower than that from the cement component. The processes of compaction and cementation were shown to be effective in reducing the leaching of salts. (Compaction also reduced radon exhalation.) It was concluded that no significant leaching of any potentially harmful component of the cement stabilized materials would occur, even where the road base was exposed to free water. The water environment under a road does not change very quickly, since the road bed has a low permeability and the road surface is designed to be impermeable.

The environmental impact of the experimental road bases constructed in Texas, USA, in the early 1990s was evaluated through TCLP analysis of the

²⁴ TCLP: Toxicity characteristic leaching procedure.



FIG. 50. Aerial view of an experimental road in central Florida, USA, showing the positions of the monitoring wells (courtesy: Florida Industrial and Phosphate Research Institute).

mixture components along with analysis of the groundwater, surface water and leachates [221]. The concentrations of leached chemicals were found to be below levels of environmental concern and in many cases negligible. In central Florida, USA, groundwater monitoring adjacent to one of the two experimental roads constructed in 1986–1987 was undertaken four months prior to construction and thereafter for 27 further months, resulting in a total monitoring period of 31 months [230]. Follow-up monitoring continued until 2008. The positions of the monitoring wells relative to the road are shown in Fig. 50. No significant impact on the groundwater was detected, with the concentrations of leached chemicals all remaining below levels of environmental concern [231].



FIG. 51. Monitoring of gamma radiation above an experimental road in Florida, USA (courtesy: Florida Industrial and Phosphate Research Institute).

Groundwater monitoring of the second of the two experimental roads constructed in 1986–1987 was carried out in a similar manner and, again, the experimental road was found to have no measurable impact on the quality of the groundwater.

10.5.3.3. Radiological impact

The two experimental roads constructed in Florida, USA (see Section 10.5.3.1), were subjected to a radiological assessment by monitoring the air, soil and groundwater before and after construction [230]. The monitoring addressed gamma radiation (see Fig. 51), outdoor radon and ^{226}Ra in samples of water and soil. From the results of gamma exposure measurements, it was determined that the absorbed dose rates 1 m above the paved road surface were 0.015–0.035 $\mu\text{Gy/h}$ higher than pre-construction values and did not change appreciably over time. These incremental dose rates are within the normal range of variability of background levels. The radon concentrations measured in the air and soil after construction were not significantly different from those measured before construction [232]. The same was found to be the case for the activity concentrations of ^{226}Ra measured in the groundwater (over a one year period) and the soil around the experimental roads. It was concluded, therefore, that the construction of the roads had had no appreciable effect on radon and ^{226}Ra levels in the surrounding environment.

Gamma radiation monitoring was also carried out above an experimental road surface made from roller compacted concrete containing phosphogypsum (described in Section 10.5.3.1) [229]. The absorbed dose rate 1 m above the road

surface was determined to be 0.009 $\mu\text{Gy/h}$, about 50% lower than that recorded above a nearby asphalt road (0.020 $\mu\text{Gy/h}$) and about 25% lower than that recorded above a nearby non-paved surface (0.012 $\mu\text{Gy/h}$).

10.5.4. Marine applications

Many phosphogypsum stacks are located around low lying coastal areas and the use of this phosphogypsum in marine applications is therefore an attractive proposition from an economic point of view. Marine applications of phosphogypsum offer many potential benefits, including the stabilization of vulnerable coastlines, the protection of areas such as coastal wetlands against the risk of flooding and the re-establishment of coastal industries such as shellfish production.

Research has focused on the stability of mixtures of phosphogypsum, fly ash and cement in seawater environments and their effect on the surrounding marine environment, with particular attention being given to the suitability of such mixtures for making oyster cultch or artificial reefs [233–239]. Mixtures containing various proportions of phosphogypsum (55–73%), cement (2–10%) and fly ash (25–42%) have been found to suffer little degradation in sea water over periods of up to two years. A key factor in creating resistance to degradation in sea water and reducing the diffusion of heavy metals and ^{226}Ra is the formation of a calcite (CaCO_3) surface layer that acts as a physical barrier to seawater intrusion. The inclusion of fly ash in the stabilized phosphogypsum mixture promotes the formation of such a layer while limiting the required cement content to only 2–3%. The leaching of heavy metals and ^{226}Ra from stabilized phosphogypsum is comparable with that from pure cement and well below levels that might be of concern for health. Tests in the field have shown that stabilized phosphogypsum mixtures are capable of supporting the growth of oysters and other shellfish and do not lead to any significant bioaccumulation of heavy metals in fish.

10.5.5. Landfill

Phosphogypsum has been shown to have good potential for use as a cover material in landfill disposal facilities [240–242]. In Italy, phosphogypsum has been used experimentally as a liner for landfill on the edge of the Venice lagoon [243]. Laboratory studies and pilot scale testing indicate that the sulphur in the phosphogypsum increases the biological activity in the buried refuse. The increased rate of degradation allows 30–45% more waste to be buried in a given volume of landfill, thus considerably extending the useful life of the facility. Since an industrial landfill facility is designed to isolate the waste from the surrounding environment, for instance through the use of an impervious liner, it is highly unlikely that the additional amounts of heavy metals and ^{226}Ra introduced

through the phosphogypsum would lead to any significant environmental or radiological impact.

10.5.6. Sulphur recovery

The use of phosphogypsum as a source of sulphur has been studied extensively. Many process routes, both chemical [244–249] and biological [250–252] have been explored, but all require considerable energy inputs. With the availability of low cost by-product sulphur from the oil and gas industry, the recovery of sulphur from phosphogypsum is unlikely to be competitive from a purely economic point of view. However, because of the considerable financial implications associated with the continued storage of phosphogypsum in stacks, the use of phosphogypsum as a source of sulphur could become worthwhile from a broader perspective, particularly since, in the chemical recovery process, the radionuclides in the phosphogypsum appear to migrate to the calcium carbonate by-product, leaving the ammonium sulphate intermediate product free of radioactivity [253]. The radiological aspects of biological recovery processes have not been studied, but it can be expected that the radionuclides would remain in the residue after removal of the sulphur content, leaving the sulphur essentially free of radioactivity.

10.5.7. Other uses

Phosphogypsum has many other uses that have proven to be successful and economic, although the amounts of material involved are generally small. Such uses include:

- (a) Treatment of industrial waste:
 - (i) Bauxite waste [254];
 - (ii) Coal mining waste (removal of barium and radium) [255];
 - (iii) Metal finishing waste [256];
 - (iv) Textile waste (removal of colour and organics) [257].
- (b) Agricultural applications:
 - (i) As a binder for fertilizer [258];
 - (ii) As an additive to bauxite residue for use in improving phosphorus retention in sandy soil [259].
- (c) As an additive for improving the performance of bauxite residue drilling mud [260].
- (d) As a filler for ‘plastic wood’ [261].
- (e) As a de-icing additive [262].

10.6. DISPOSAL OF PHOSPHOGYPSUM

The rate at which phosphogypsum is produced far exceeds the rate at which it is used. In addition, very large stockpiles of phosphogypsum from past production are held in indefinite storage in stacks (see Section 10.1). Unless this phosphogypsum can be put to good use in the foreseeable future, the need for the disposal of large amounts of phosphogypsum will remain. The most common methods of disposal are in situ disposal through stack closure and discharge to water bodies as a dilute slurry. Relatively small amounts of phosphogypsum are also disposed of by backfilling in mined-out areas.

10.6.1. In situ disposal through stack closure

10.6.1.1. Evolution of the approach to closure

The worldwide trend has been for production facilities to become consolidated, resulting in significant increases in production capacity. This has created a tendency to close older, smaller phosphogypsum stacks and to plan for a smaller number of very large ones. As an example, an older type of stack was closed on the edge of Tampa Bay in Florida, USA, in 1992. At the time of closure, the stack covered a land area of 138 ha and its height was 66–69 m. During operation, it was growing in height at a rate of about 6 m per year [263]. Some older stacks were not formally closed, having been abandoned by their owners, and have tended to blend into the landscape over time as a result of local vegetation establishing itself on the stack surface.

Stack closure has become significantly more common in major production centres such as those in Florida, USA, as the industry scales back production or stacks reach their maximum usable height. The closure process in Florida is subject to a formal procedure involving the establishment of detailed specifications and resulting in a published plan, usually subdivided into phases [264, 265]. The Tampa Bay stack closure [263] was completed in just over a year (1992), while a stack at Piney Point required more than two years to close [266].

Although closures of production facilities have become more commonplace since the 1990s, closure of the associated stacks has tended to be carried out in an unplanned or unforeseen way, often as a consequence of the bankruptcy of the producing company. There has been a lack of forward planning, particularly where the closure of production facilities has marked the end of national production capacity. Owing to inadequate communication within and between countries, the lessons learned from stack closure at one site have not been transmitted to other sites. Instead, the approach to stack closure has been ad hoc in nature, resulting in inconsistency between sites and unnecessarily high costs.

The situation is now changing, however. At some sites, such as that at Huelva, Spain, planned closure is now being pursued actively, leading to the emergence of some best practices that could beneficially be passed on to other sites in due course.

For new production facilities, the adoption of a complete life cycle approach, in which eventual stack closure forms an integral part of the planning of the facility, brings substantial benefits. These include reduced financial and environmental burdens and better prospects for the eventual use of the phosphogypsum, the pond water and the land (thus offsetting the costs of stack closure). One of the many implications of such an approach is that it would put an end to the common practice of burying waste indiscriminately in the stack with no records and, instead, lead to the implementation of a standard operating procedure that designates specific areas for burial with an associated long term management plan. In terms of the life cycle approach, any new facility would have in place, from the outset, a clear plan for stack closure that would be sufficiently detailed to enable the proper financial provision to be included in the planning of the facility as a whole. Lessons learned at facilities such as Gela, Italy, and Piney Point, USA, have shown that the magnitude of this financial provision could be very large. This could have significant implications for countries building production facilities for the first time or which are significantly increasing their current levels of production. The large capital investment required to establish a facility combined with the need to make adequate provision for closure costs could threaten the success of the business enterprise from the outset. This underlines the need for making sensible and well thought out policy and regulatory decisions so that these ‘negative externalities’ are no greater than they need to be.

10.6.1.2. The closure process

The older the stack, the more likely is the occurrence of problems in the closure process, especially problems related to the very large volumes of process water contained on top of, or within, the stack. Closure activities associated with the stack itself and with the stored process water are interdependent. When the storage capacity of a phosphogypsum stack is exhausted or when a production facility is permanently closed, not only the pond water but also the seepage and rainfall runoff have to be contained within the site and/or treated before discharge. This has to continue for as long as rainwater is able to infiltrate the stack and/or until the water in the pores of the phosphogypsum has drained out. In addition, prolonged rainwater infiltration will produce a network of dissolution cavities that could make it more expensive to cap the stack at a later date.



FIG. 52. A computer modified image of the regrading of a stack as part of the closure process (courtesy: Fertiberia, Spain).

Regrading and revegetation of the side slopes, after any necessary surface treatment with dolomitic limestone to rectify magnesium deficiency in the topsoil, may often be sufficient to prevent rainfall (and snow melt) from seeping into the slopes and may thus allow for subsequent runoff to be discharged from the site without treatment. Under favourable climatic conditions and hydrogeological settings, regrading of the top of a gypsum stack to promote surface runoff in combination with good vegetation and/or a relatively impervious clay cover may be sufficient to prevent rainfall infiltration. In other situations, capping with an impervious geosynthetic barrier may be needed. A stack undergoing regrading is shown in Fig. 52.

Revegetation of phosphogypsum stacks is greatly facilitated by the fact that phosphogypsum performs well as a soil. An example of revegetation at a site in Italy is shown in Fig. 53. At this site, stack closure was carried out as part of the total decommissioning of the phosphoric acid production facility — this is possibly the first global example of such an integrated approach to decommissioning and closure. The integrated approach also opens up the possibility of controlling the sequence of activities such that the process equipment in the plant can be used to facilitate stack closure. At the Piney Point facility in Florida, USA, for instance, the cost of stack closure was reduced by redeploying equipment in the phosphoric acid plant to treat the acidic pond water instead.



FIG. 53. Planned revegetation of a stack at Gela, Italy.

Once infiltration into the stack has been eliminated, the stack will continue to drain until any settling due to consolidation and creep is complete and the moisture in the phosphogypsum pores reaches its maximum retention capacity. Overall, drainage depends on the dimensions and age of the stack, the properties of the phosphogypsum and the hydrogeological setting. A stack constructed on porous ground will drain much more rapidly than one constructed on low permeability clay.

10.6.1.3. Removal of closed stacks

Stack closure is not an irreversible process and it is, therefore, possible for all or part of the phosphogypsum contained within a closed stack to be subsequently retrieved for use. One important consideration in the reopening of a closed stack for this purpose is the presence of other waste materials within the stack that may have significant levels of contamination. One option is for these materials to be reburied within the remnants of the stack. Alternatively, they may be transported to another disposal site.

A stack may also be removed in order to make use of the land on which it stands. The spread of urban development is bringing populated areas ever closer to older stacks, many of which are no longer in operation. Examples of this



FIG. 54. New housing development next to a phosphogypsum stack at Gela, Italy.

situation can be found in Greece, Italy (see Figs 54 and 55) and Spain (see Fig. 56). In Greece, the city of Athens has actually engulfed a stack associated with a former production facility, with only the surface of the stack itself remaining free of buildings. Owing to the growth in real estate values at many of these sites, there is increasing interest in removing some of these older stacks and remediating the land for development. Developers have indicated an interest in removing a stack at Thessaloniki, Greece, in order to develop the site for residential purposes. A similar situation exists in the Tampa Bay region of Florida, USA, where property developers are seriously evaluating the costs of remediating contaminated sites to enable their use for residential development. Production facilities are often situated in coastal areas that have become increasingly prized by property developers. These sites may offer a good financial return if they can be brought back into consideration for building purposes, especially residential housing. The freeing of land for public use by stack removal has already brought community-wide benefit, as illustrated by examples in Athens, Greece [267], and Sfax, Tunisia [268], where new recreation facilities have been established on the remediated sites. More information on the remediation of a phosphogypsum stack in Tunisia is provided in Annex II.



FIG. 55. Commercial buildings next to a phosphogypsum stack at Gela, Italy.



FIG. 56. The edge of a phosphogypsum stack at Huelva, Spain, with the city of Huelva close by.

10.6.1.4. Radiological aspects

The closure of a stack, when conducted in a planned and effective manner, ensures that any future migration of potential pollutants, such as acidic water, heavy metals and radionuclides, remains at acceptably low levels. Thus, the radiological impact on members of the public living nearby is insignificant. Extensive monitoring carried out over many years at over twenty sites in Florida indicated that radionuclide discharges from stacks and migration to groundwater are insignificant [81]. Operating experience also suggests that doses to the public from legacy sites are negligible. Many older stacks that have already been closed are legacies of former production operations and may not have been closed in accordance with current standards. In such cases, the radiological (and non-radiological) impacts may be greater than those considered acceptable in terms of current standards. Where this is found to be the case, a decision on possible remediation (or removal) would have to be taken by the relevant national authority, bearing in mind that the costs involved could be very high.

10.6.2. Discharge to water bodies

It has been estimated that, up to 2006, a worldwide total of 1.8–3.0 billion t of phosphogypsum had been disposed of by discharge to water bodies, representing 29–50% of all phosphogypsum produced up to that time (see Table 32). This form of disposal was at one time practised widely in Europe. However, as a result of the progressive imposition of legal restrictions on this form of disposal, most phosphoric acid production in Europe (and thus the discharge of phosphogypsum) has now ceased. The situation in the USA and China has been much the same. Discharges to water bodies are currently running at about 31 million t per year, representing 19% of the total amount of phosphogypsum produced annually worldwide. All of these discharges occur in countries outside Europe and the USA, where, on average, they account for about 30% of those countries' current phosphogypsum production. Further information on discharges of phosphogypsum to water bodies is given in Table 36.

The discharge of phosphogypsum as a dilute slurry to the sea has been practised on a large scale by phosphoric acid production facilities situated at coastal locations. In principle, given appropriate conditions in the receiving waterbody, the environmental impact of this form of disposal is apparently negligible. Such conditions were not considered to prevail in the case of discharges to water bodies such as the Irish Sea, the North Sea and parts of the Mediterranean, however, and such discharges have now ceased [269]. For example, discharges into the North Sea from a phosphoric acid facility at Sellafield, UK, were found to have led to the uptake of radionuclides by marine

TABLE 36. DISCHARGE OF PHOSPHOGYPSUM TO WATER BODIES, BY COUNTRY

Country	Status of discharges
Canada	Former discharges to the bay and inland sea have now ceased.
China	25% of phosphogypsum was discharged to rivers. Discharges have now ceased.
France	Significant discharge to the river in the past and now ceased.
Lebanon	Discharges to the sea.
Morocco	All phosphogypsum is discharged to the sea. The policy for future discharges is under review.
Netherlands	All phosphogypsum was discharged to estuaries. Discharges ceased in 2001 owing to the closure of the plant because of the costs of regulatory compliance.
South Africa	Significant discharge of phosphogypsum to the sea.
Spain	20% of phosphogypsum was discharged to a river estuary. Discharges ceased in 1988.
Tunisia	Progressive termination of discharges to the sea. Discharges planned to cease entirely in 2012.
UK	All phosphogypsum was discharged to the sea. Discharges ceased in 1992, largely because of the costs of regulatory compliance.
USA	An estimated 23% of the phosphogypsum produced up to 1981 (500 million t) was discharged to rivers and to the sea. Discharges ceased in 1982.

food sources [86]. In the light of experience such as this, and because of heightened sensitivities about pollution of the marine environment in general, the discharge of phosphogypsum to the sea is widely regarded as environmentally unacceptable and in contravention of international agreements. In most countries, legislation now prohibits such discharges and the resulting financial consequences have caused many facilities to close down. As a result of these developments, discharges of phosphogypsum to the sea have, since the 1990s, been progressively curtailed [33].

A similar situation exists for discharges to other large water bodies. Discharges to major rivers such as the Yangtse in China or the Mississippi in the USA²⁵, as well as to estuarine environments such as that at Huelva, Spain, have ceased. Follow-up studies based on field measurements made at Huelva have indicated that, once the discharge ceases, the self-cleaning properties of flowing

²⁵ A phosphoric acid production facility near Taft, Louisiana, discharged phosphogypsum directly into the Mississippi River from the 1960s to the mid-1980s.

or tidal waters can be expected to reverse the buildup of contamination back to natural background levels [270–272]. The situation at Huelva is, however, influenced by the presence of an operational phosphogypsum stack that potentially acts as an ongoing source of contamination of the estuary. The evidence suggests that, because of this, the contamination levels in the estuary, while reducing gradually, may remain elevated above background levels for some time [273]. In a study carried out by the European Commission on radionuclide discharge from the phosphate industry to north European marine waters [269], estimated discharges of 65 TBq of ^{226}Ra and ^{210}Po , together and 32 TBq of ^{210}Pb , were reported for a period of more than two decades of operation. Analysis of several marine species indicated increased accumulation of ^{210}Po , possibly attributable to discharges. Probably as a result of closure of some of the industries and technological improvements in existing processing plants, a downward trend in activity discharges was noted.

10.6.3. Backfilling into mined out areas

The pits created by the mining of phosphate ore may, in some instances, be remediated by backfilling with a blend of clay tailings from the beneficiation process and phosphogypsum obtained directly from the filtration system of the phosphoric acid plant. The high calcareous content of the clay neutralizes the acid retained within the phosphogypsum. Such an approach has been adopted at a facility in North Carolina, USA, where a unique set of hydrogeological conditions favour this method of disposal.

10.7. REGULATORY CONSIDERATIONS

The storage of phosphogypsum in stacks, irrespective of its radioactivity content, creates potential environmental and physical safety hazards and, therefore, needs to be controlled by the relevant authorities in a consistent and harmonized manner. Similar controls are necessary when a stack is undergoing closure. Evidence shows that, with such controls in place, there is no necessity for additional regulation for purely radiological purposes. Future liabilities associated with the continued presence of large phosphogypsum stacks place a considerable burden on future generations. This, together with the increasing rate of phosphogypsum production, provides a very compelling reason for creating a regulatory environment that is conducive to identifying and promoting further ways of safely using phosphogypsum as a co-product of phosphoric acid production rather than having to manage it as waste.

For the foreseeable future, the discharge of phosphogypsum to water bodies is largely being phased out but is likely to continue in some countries. Experience has shown that, to ensure acceptable levels of risk to humans and to the environment, such discharges would need to be regulated as part of an authorized practice on the basis of a situation specific risk assessment.

All evidence suggests that the doses received as a result of the use of phosphogypsum in agriculture, road construction, marine applications and in landfill facilities are sufficiently low that no restrictions on such uses are necessary. The uses of phosphogypsum in structural panels for the construction of a house could, in extreme circumstances, result in the occupant receiving an annual effective dose exceeding 1 mSv. Therefore, it would be prudent for the relevant authority to ensure that an appropriate situation specific risk assessment be carried out in order to determine whether any restrictions on this particular use of phosphogypsum are needed. For all other uses of phosphogypsum in home construction, including its use in cement, bricks, plasterboard and tiles, the annual effective dose received by the occupant is unlikely to exceed 1 mSv and restrictions on such use would appear to be unnecessary.

11. DECOMMISSIONING OF WET PROCESS PLANTS AND MANAGEMENT OF SCRAP

Given the substantial capital investment needed to construct wet process facilities, the plants are usually operated for very long periods. Some plants have been in continuous use for well over 50 years and have been in a state of continuous maintenance because of corrosion and the formation of scale and sediments. During the course of routine operations, production is suspended for short periods to allow critical items such as pipes and filter cloths to be cleaned or replaced. Thus, scrap materials are generated throughout the life of the plant, as well as during the eventual decommissioning process. With the possible exception of the decontamination of the land on which the facility is situated, the issues addressed during routine maintenance tend to be similar to those addressed during the decommissioning process.

11.1. DECOMMISSIONING

Considerable knowledge and experience is being established in connection with the ongoing decommissioning of wet process plants, notably in Western

Europe, where production in most countries has ceased. Examples include plants in France, Italy [31], Greece [274], Netherlands [66] and the UK [68], which were forced to close as a result of new legislation that prohibited the discharge of phosphogypsum to water bodies. In order to continue operating, these plants would have been required to store phosphogypsum in stacks, a process that would have been prohibitively costly and in some cases not even possible because there was no available land on which to locate the stacks. Two such plants are shown in Figs 57 and 58. Usually, decommissioning is carried out as part of the permanent closure of the production facility, in which case the decommissioning process covers the decontamination and dismantling of the plant together with the remediation of the site. There are exceptions, however:

- (a) While decommissioning typically includes the dismantling of a plant, or part thereof, a facility may be decommissioned without dismantling. In such instances, after decontamination, the existing or modified structure may be put to another use.
- (b) Sometimes, an old plant may be decommissioned so that it can be replaced by a new plant on the same site. In such situations, it is now common practice to address issues such as soil contamination as part of the rebuild rather than deferring them to the time of final closure of the facility.

Normally, the decommissioning process is planned as part of the orderly termination of the business. Sometimes, however, the process is unplanned because outside intervention has become necessary following a failure of the business. In such cases, bearing in mind that an abandoned plant deteriorates rapidly, decommissioning may have to be carried out urgently.

11.1.1. Development of the decommissioning plan

The first step in the decommissioning process is the development of a decommissioning plan. This plan sets out the necessary sequence of administrative and technical actions leading to the eventual removal of some or all of the regulatory controls applied to the facility during its operation. The plan also sets out the necessary policies and procedures, which typically include the following:

- (a) A health and safety policy, with allocation of roles and responsibilities;
- (b) An outline procedure for dismantling the installation, with flowsheet and timeline;



FIG. 57. A deteriorating phosphoric acid plant awaiting dismantling.



FIG. 58. A wet process plant at Gela, Italy, during decontamination and dismantling.

- (c) Procedures for the flushing of process lines, the cleaning of vessels and the categorization of wastes as hazardous, radioactive or mixed;
- (d) Standard operating procedures for contractors and third parties, with training and certification requirements as appropriate;
- (e) A methodology for the treatment, transport and disposal of scale, other radioactive material and radioactively contaminated equipment, including the necessary documentation;
- (f) Contingency arrangements.

The decommissioning plan is based on a comprehensive radiological survey that identifies the location of radioactive material and the resulting exposure levels over the whole site, including peripheral areas used for activities such as transport, cleaning, repair and maintenance. The activity concentrations of radionuclides in environmental media such as water, soil and crops may have to be measured in areas surrounding the site to determine any contamination via airborne dust or entry into water courses. In addition, the survey needs to identify the radiological situation that will prevail during the decommissioning process itself as a result of the presence of radioactive material and contaminated equipment associated with decontamination and waste management activities.

The decommissioning plan incorporates a detailed description of the facility, including a history of operations at the site compiled from official records and, where appropriate and feasible, from worker interviews. A detailed knowledge of these aspects helps to ensure not only that the radiological objectives of the decommissioning process are achieved but also that the scale and cost of the decommissioning process do not extend beyond what is really necessary. The following historical aspects are typically documented:

- (a) All known industrial activities carried out on the site since the land was first occupied and developed;
- (b) The process steps in which radioactive material was handled, the locations of the pipes, pumps, valves, tanks and storage areas involved, and the activity concentrations of the materials concerned;
- (c) As full a description as possible of plant modifications and changes of ownership;
- (d) Known leakages, spillages and movement of radioactive material, including transfers from storage for onward transport and transfers to impoundment areas.

The plan addresses each aspect of the decommissioning process in a level of detail commensurate with the degree of radiological hazard. As a plant undergoing decommissioning is likely to have been in operation for a long time, often with imperfect documentation and record keeping, it can prove difficult to anticipate exactly the location, nature and extent of radioactive deposits and soil contamination that have accumulated over the years of routine plant operation. For this and other reasons, the plan may have to be adjusted in response to unforeseen events as the decommissioning process proceeds.

The decommissioning plan quantifies the likely environmental impacts of the decommissioning process and the risks (both radiological and non-radiological) to workers engaged in the decommissioning work and to members of the public. In this regard, the following process materials are typical of those that have to be considered:

- (a) Acids used in the various production processes;
- (b) Ammonia;
- (c) Hydrogen sulphide that might be present in sulphur storages;
- (d) Scale, sludge residues and other materials in which radionuclides, such as radium, and heavy metals, such as arsenic, cadmium, chromium, lead, mercury and selenium, may accumulate.

The adoption of postulated ‘scenarios’ can be useful in the planning of a decommissioning process, especially if there are major gaps in the known history of the plant. The scenario concept permits a ‘what if’ approach to the determination of hazards and risks that may be present at the site. It also facilitates future planning, including the consideration of possible future uses of the site and the likely exposure implications.

The compilation of the necessary risk assessments and other documentation is facilitated by having a comprehensive checklist of all types of equipment on the site, which may typically include:

- (a) Reactor vessels, such as the attack tank and defluorination reactor;
- (b) Storage tanks;
- (c) Buffer tanks for spilled acids;
- (d) Evaporators;
- (e) Scrubbers;
- (f) Pumps, valves and steel pipes, including rubber linings where used;
- (g) Stainless steel frames, transport reels and rubber belts from belt filters;
- (h) Seal tanks and table filters;
- (i) Filter cloths and bag filters;
- (j) Metal filter pans;
- (k) Machine frames and other metal structures;
- (l) Carbon stones and bricks from the reactor lining;
- (m) Other bricks and ceramic floor tiles;
- (n) Drains, gutters and drain wells.

The decommissioning plan sets out the training and safety procedures to be used, including the keeping of records of the training provided. The responsibility for radiation protection training is generally assigned to a designated radiation protection officer. The training of on-site personnel is of particular significance since few, if any, of these individuals are likely to have had prior experience of working in such an environment. The procedures are usually designed to ensure that work experience is formally documented in order to support a systematic learning process and to ensure that best practices developed during the course of the work are passed on to other decommissioning operations in the future.

11.1.2. Implementation of the decommissioning plan

The decommissioning process is carried out in accordance with the decommissioning plan. An operational survey may be carried out during the process in order to monitor progress and thereby identify any adjustments to the plan that may become necessary.

Data relating to the dismantling and removal of equipment and the removal of residues, including radiological data such as gamma dose rates and surface contamination levels, are fully documented as the decommissioning process proceeds. The results of the radiological measurements provide the basis for determining how to deal with the materials and equipment and, in particular, whether they meet predetermined clearance criteria and can thus be released from the site. Where provided for in the decommissioning plan, some items of contaminated equipment may be decontaminated at the site in order to bring them into compliance with the clearance criteria. Further information on the management of scrap is given in Section 11.2.

11.1.3. Final report

A final report compiled at the end of the decommissioning process provides a comprehensive record of the work carried out and the results obtained. In this way, the report provides verification that the decommissioning process was carried out according to plan and that the objectives of the process were met. The final report can also assist in the planning and execution of similar decommissioning processes in the future and is of particular value in documenting the lessons learned as a result of having to deviate from the original decommissioning plan because of unforeseen events. It is common practice for a minimum retention period to be specified for the final report, typically 15–50 years, since it may be needed in the event of any future litigation. The content of the final report is illustrated in the following example from the decommissioning of a phosphoric acid plant in the Netherlands [66]:

- (a) Historical information, documentation and references;
- (b) A summary of the decommissioning project;
- (c) A history of the organization and management of the project, including allocation of responsibilities and supervision, with comments on any variations from the initial plan;
- (d) The applicable licences;
- (e) The results of the preliminary inventory;
- (f) An overview and description of the environmental monitoring programme and procedures, with any results or findings;
- (g) An overview of the contaminated installation components that were identified;
- (h) An overview of the methods applied for treating these components;
- (i) The plan of action for each method;
- (j) An inventory of the end point disposal of contaminated components;
- (k) An overview of the release of equipment used;

- (l) A list of the tools and aids that were applied and released;
- (m) A calculation of the doses received by workers and the public, records of which are to be retained for 35 years;
- (n) An overview of the quantities and temporary storage of the radioactive waste produced;
- (o) The transfer of radioactive material to third parties for the purpose of further processing;
- (p) Remediation activities and procedures for the release of the site, with any necessary ongoing monitoring procedures.

11.1.4. Management of residues

The management of residues removed during the decommissioning of a phosphoric acid plant in Rotterdam, Netherlands, is described in Ref. [66]. The residues were categorized as either radioactive waste or chemical waste, depending on the radioactivity concentrations. These two categories of waste were managed in the following way:

- (i) Radioactive waste: Radium rich scale and contaminated carbon and rubber having a total mass of 6.7 t were removed. The total ^{226}Ra activity was 7 GBq, implying an average activity concentration of more than 1000 Bq/g. The material was packed into 118 drums of 100 L capacity and transferred to the Centrale Organisatie voor Radioactief Afval (COVRA) along with the HEPA filters²⁶ used during decontamination operations. In order to meet the COVRA specification that the liquid content be less than 1%, the waste was dried by infrared heating before packing.
- (ii) Chemical waste: Water used for high pressure water jet cleaning and having a total mass of 44 t was collected in 16 tank cars. Particles of radioactive scale were removed from the water by an industrial waste company but, because of the chemical impurities that remained dissolved within it, the water was classified as chemical waste and disposed of accordingly. The residual ^{226}Ra activity concentration was less than 1 Bq/L. A total of 750 t of phosphogypsum scale with a ^{226}Ra activity concentration of less than 1 Bq/g was also collected and classified as chemical waste.

²⁶ HEPA: High efficiency particulate air. A HEPA filter is a type of air filter that satisfies certain standards of efficiency, such as those set by the United States Department of Energy.



FIG. 59. Typical lay down area for scrap.

11.2. MANAGEMENT OF SCRAP

Various contaminated scrap items are removed from wet process plants during periods of maintenance carried out as part of routine plant operation and during the eventual plant decommissioning process. Decontamination of these items can greatly facilitate the management of this scrap and opens up repair or recycling options that might not otherwise be available. In many cases, however, decontamination is not technically or economically feasible and the scrap, therefore, has to be managed as radioactive material. Many contaminated items take the form of metal components such as structural steel, gratings, pipes, valves, filter pans and vessels, for which refurbishment, repair or recycling by melting are often worthwhile options. If the metal is recycled by melting, the need for decontamination of the scrap metal can usually be avoided.

Generally, each site has designated 'lay down' areas for collecting and segregating scrap items and measuring their surface contamination levels (see Fig. 59). Items are segregated according to the route by which they will be managed. There are four main options for managing scrap at wet process plants:



FIG. 60. Scrap designated for recovery of the metal content by melting.

- (i) Off-site repair by a service company;
- (ii) Off-site recovery of the metal by melting (see Fig. 60);
- (iii) Off-site disposal in an industrial or hazardous waste landfill facility (see Fig. 61);
- (iv) On-site disposal by burial, for instance in the phosphogypsum stack (see Fig. 62).

Procedures for the radiological monitoring of scrap leaving the facility tend to vary. Some facilities routinely monitor individual items of scrap before they are loaded for transport. Other facilities rely on portal monitors located at the exit from the site to survey loaded trucks before departure.

11.2.1. Decontamination of scrap

There are significant variations in the types of contaminant and their radionuclide concentrations. Although vigorous washing is sometimes sufficient for removing surface contamination, techniques based on water jetting, chemical treatment or mechanical abrasion are usually necessary for removing more persistent contamination, such as the scale deposited in wet process plants.



FIG. 61. Scrap designated for off-site disposal at a landfill facility.



FIG. 62. Scrap designated for on-site disposal by burial.

Components that come into contact with acid are often protected by a rubber lining, which becomes progressively contaminated during plant operation. Rubber belts from belt filter systems also become contaminated. In Florida, USA, the contaminated surface layer of a long rubber belt from the belt filter system, including the accompanying transportation reel, was successfully abraded away using high pressure water jetting with a suitable combination of nozzles, pressure and water volume [53]. High pressure water was also used to decontaminate the rubber linings of the attack tank and the acid storage tank in a phosphoric acid plant, using remotely controlled jetting equipment and a suction system to remove and conserve the contaminated water. The mist generated during the decontamination operation was removed via a filter system. The water–air mixture was discharged using a demister and a high performance filter, thus minimizing any migration of radioactivity to the environment. Decontamination of rubber components is not always the chosen option, however. In the decommissioning of a phosphoric acid plant in the Netherlands [66], contaminated rubber was removed together with radium rich scale during dismantling of the plant. In this instance, the rubber was not decontaminated but, instead, was sent with the scale to a radioactive waste storage facility (see Section 11.1.4).

11.2.2. Management of contaminated scrap

Measurements were made on a large variety of scrap items at seven wet process facilities in Florida, USA, over the course of a year [275]. The total ^{238}U and ^{226}Ra activities contained within the items sampled were 106 and 322 MBq, respectively, and the total mass was 66 t. The mean activity concentrations were, thus, 1.6 Bq/g for ^{238}U and 4.9 Bq/g for ^{226}Ra . An analysis showed that more than half of the uranium activity resided in scrap destined for off-site disposal at landfill facilities (see Fig. 63), while 78% of the radium activity resided in scrap destined for burial at the site, usually in a phosphogypsum stack (see Fig. 64). Only a third of the items destined for off-site recycling or disposal exhibited gamma dose rates above background levels. For the four scrap management options (off-site repair, off-site metal recovery by melting, off-site disposal at a landfill facility and on-site disposal by burial), the situation could be summarized as follows:

- (i) Only a few items were destined for off-site repair. These were decontaminated before leaving the site and were, therefore, excluded from the radiological analysis.

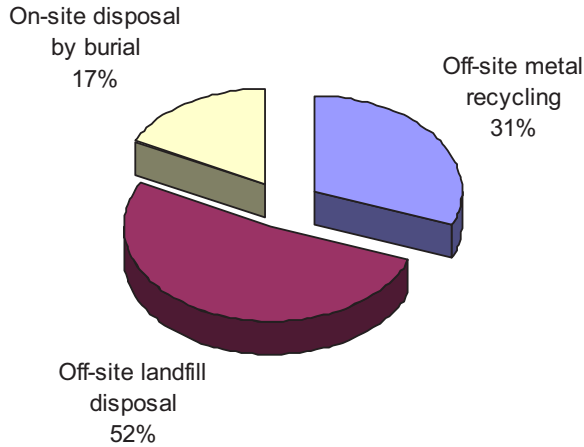


FIG. 63. Destination of ^{238}U activity in scrap arising from facilities in Florida, USA.

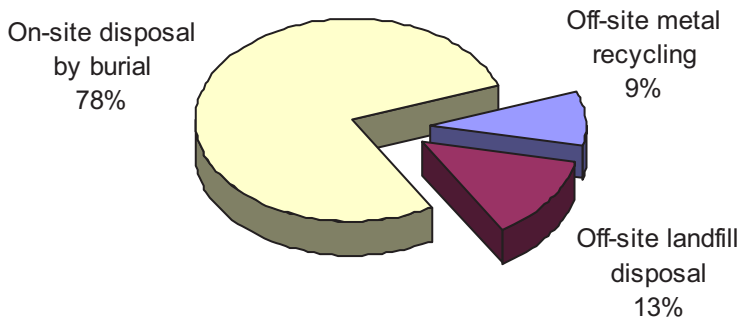


FIG. 64. Destination of ^{226}Ra activity in scrap arising from facilities in Florida, USA.

- (ii) Most of the scrap metal (26 t) was sent to off-site metal recycling facilities. The mean activity concentrations of ^{238}U and ^{226}Ra were about 1.25 and 1.1 Bq/g, respectively.
- (iii) The scrap sent for off-site disposal in landfill facilities (22 t) consisted predominantly of paper, cardboard and plastic. The mean activity concentrations of ^{238}U and ^{226}Ra were about 2.5 and 2 Bq/g, respectively.
- (iv) The scrap retained for burial on-site consisted predominantly of process components such as filter cloths and fibreglass having little value for recycling. The mean activity concentrations of ^{238}U and ^{226}Ra were about 1 and 14 Bq/g, respectively.

During the decommissioning of a phosphoric acid plant in Rotterdam, Netherlands [66], the following contaminated steel components were identified as suitable for recycling by melting:

- (a) Parts of the tilting-pan filter;
- (b) All steel pipes, including rubber linings;
- (c) Vacuum seal tanks;
- (d) Separators;
- (e) Buffer tank.

The total activities of ^{226}Ra and ^{210}Pb contained within these items were 1.9 and 0.5 GBq, respectively, and the total mass was 62 t. The mean activity concentrations of ^{226}Ra and ^{210}Pb were, thus, about 30 and 8 Bq/g, respectively. The items were packed into seven closed IP-1 containers and transferred to a specialized melting facility. Objects that were too large, such as tanks, were cut into pieces before being packed.

11.3. OCCUPATIONAL EXPOSURE

The various decommissioning tasks are usually carried out according to standard operating procedures in order to ensure the effectiveness of the work and the safety of the workers involved. Health and safety precautions are incorporated into these procedures to ensure compliance with local OHS laws and regulations. Such precautions help to minimize the radiation exposure of workers. Similar considerations generally apply to the management of scrap.

Depending on the levels of exposure to radioactive material, decommissioning and scrap management work may have to be carried out in accordance with an appropriate radiation protection programme, as described in Ref. [4]. The requirements embodied in the radiation protection programme are likely to include the wearing of personal monitoring devices by selected workers to determine external exposure to gamma radiation and/or internal exposure from the inhalation of radionuclides in airborne dust. Both types of exposure can be significant because of the close proximity of workers to scale and other material with high radionuclide activity concentrations and because of the generation of airborne dust during welding, cutting, dismantling and decontamination activities. The potential for exposure is of particular concern when carrying out dismantling and decontamination work in confined areas such as tanks, especially when dry decontamination methods such as mechanical abrasion are used. During work of this nature, it is common for respiratory protection to be required as part of the standard OHS procedures and, in addition, exposure periods may

have to be restricted. The use of high pressure water as an alternative to dry decontamination techniques, especially when, in confined areas, it is controlled remotely, as described in Ref. [53], is not only very effective in removing stubborn contamination but also considerably reduces the potential for exposure.

The decommissioning of a phosphoric acid plant at Rotterdam, Netherlands is described in Ref. [66]. The mean effective doses received by decommissioning workers over the duration of the decommissioning process are given in Table 37.

There is no published information on doses arising from the melting of scrap from wet process plants. However, a good estimate can be derived from the results of a detailed dose assessment conducted on an experimental melt of 38 t of uranium contaminated steel scrap from the South African gold mining industry [276]. The radioactivity levels in this scrap were similar to those reported in Ref. [275] for scrap from wet process facilities in Florida. The assessment of worker doses was based on the activity concentrations measured in the various process materials and in the air breathed by the workers. It was found that the inhalation of dust accounted for 96–100% of the dose. By making upward adjustments²⁷ to the South African results to account for differences in the activity concentrations of individual radionuclides in the uranium decay series, doses from the melting of metal scrap from wet process facilities were estimated and are given in Table 38. The mean annual committed effective dose for each category of worker is less than 1 mSv. The worker receiving the highest dose is the scrap processor. This worker operates the machinery for segmenting the scrap into sizes suitable for the furnace, a dusty operation involving exposure to airborne particles of contaminant during the full work period, assumed to be 2000 h/a. Should the contaminated scrap be mixed with uncontaminated scrap at the melting facility, some of the doses will, of course, be commensurately lower.

TABLE 37. DOSES RECEIVED BY WORKERS IN THE DECOMMISSIONING OF A PHOSPHORIC ACID PLANT [66]

Worker category	Mean effective dose (mSv)
Wet decontamination workers	1.2
Dry decontamination workers	<LLD ^a
Dismantling and construction workers and their assistants	<1.7
Supervisors	<LLD

^a LLD: Lower limit of detection.

²⁷ These upward adjustments were 22% for contaminant particles, 69% for slag particles and 45% for flue gas particles.

TABLE 38. DOSES EXPECTED TO BE RECEIVED BY WORKERS IN THE MELTING OF METAL SCRAP FROM WET PROCESS FACILITIES
(derived from Refs [275, 276])

Worker	Mean annual committed effective dose (mSv)		
	Gamma radiation	Dust inhalation	Total
Scrap loader	0.0006	0.40	0.40
Truck driver	0.0002	Negligible	0.0002
Scrap processor	0.0001	0.99	0.99
Furnace operator	0.005	0.43	0.43
Casting worker	0.00003	0.30	0.30
Slag worker	0.02	0.52	0.55
Crane operator	0.0002	0.39	0.39

11.4. PUBLIC EXPOSURE

Since members of the public do not normally have access to sites on which decommissioning is being carried out, the potential for public exposure is very low. During the decommissioning of a phosphoric acid plant at Rotterdam, Netherlands [66], the annual effective dose received by the most highly exposed member of the public outside the facility was determined to be less than 0.4 μ Sv over the duration of the decommissioning process.

Doses received by members of the public as a result of the landfill disposal of scrap from wet process plants are likely to be insignificant. The mean radionuclide activity concentrations in the scrap are not expected to exceed 2–3 Bq/g and the possibility of any significant external and internal exposure is very small because the material is buried under controlled conditions designed to isolate the waste from the surrounding environment.

The doses received by members of the public as a result of exposure to steel recycled from wet process facilities have been estimated by considering the radioactivity content of uranium contaminated scrap originating from facilities in Florida, USA [275], together with the results of the dose assessment for steel recycled from similar scrap originating from mining activities in South Africa [276]. Allowances have been made for differences in radionuclide concentrations, principally the higher ^{226}Ra content in the scrap from Florida. In the original dose assessment carried out for mining scrap, the doses resulting from exposure of the public to gamma radiation from various steel products were calculated. It was found that the products giving rise to the highest doses were

reinforcing bar for use in buildings and large foundry products such as components of large earthmoving equipment (the operators of which could be regarded as members of the public). The corresponding doses for steel recycled from wet process facilities are given in Table 39. The annual doses are all far below 1 mSv. In reality, it is unlikely that the steel used for product fabrication will originate entirely from contaminated scrap. Mixing with uncontaminated steel will take place either before or after the melting process. Consequently, the doses received by members of the public can be expected to be lower than those given in Table 39.

11.5. REGULATORY CONSIDERATIONS

The radionuclide concentrations in the materials encountered during the decommissioning of wet process plants and the management of scrap are frequently above 1 Bq/g and such activities clearly have to be considered for regulation as a practice. There is a potential for high occupational exposure to gamma radiation and radionuclides in airborne dust owing to the close proximity of workers to materials with elevated activity concentrations and the nature of the tasks involved in dismantling and decontamination operations. Moreover, residues designated as waste may need to be disposed of in a controlled manner in hazardous waste facilities. Nevertheless, annual doses received by decommissioning and scrap management workers appear to be below 1 mSv and doses received by members of the public are insignificant. It is important to bear in mind that standard procedures, particularly for decommissioning activities, generally incorporate health and safety precautions that are mandatory in terms of local OHS laws and regulations. While a formal radiation protection programme

TABLE 39. DOSES EXPECTED TO BE RECEIVED BY MEMBERS OF THE PUBLIC FROM EXPOSURE TO STEEL MADE FROM RECYCLED SCRAP DERIVED FROM WET PROCESS FACILITIES
(*derived from Refs [275, 276]*)

Material	Gamma dose rate (μSv/h)	Annual exposure period (h)	Annual effective dose (mSv)
Reinforcing bar used in walls	0.014	1500	0.02
Reinforcing bar used in floors and ceilings	0.025	1500	0.04
Large foundry products	0.057	2000	0.11

may be desirable or necessary in some situations, it may not always be necessary to introduce additional regulatory controls specifically for purposes of radiation protection. The most appropriate regulatory option is likely to be a requirement for authorization in the form of a registration.

Residues arising from decommissioning and decontamination activities, while generally having elevated radionuclide activity concentrations of up to a few becquerels per gram, are, in most cases, likely to remain outside the scope of the Transport Regulations.

12. EXTRACTION OF URANIUM FROM PHOSPHORIC ACID

Phosphoric acid was once an important source of uranium [277], but subsequently, during the slump in uranium prices in the 1980s and 1990s, uranium extraction at phosphoric acid plants declined to the point where, from 1997 onwards, no further production is known to have taken place. Now, as a result of more favourable attitudes towards nuclear power and the depletion of uranium stockpiles, the price of uranium has recovered significantly and there is considerable interest once again in extracting uranium from phosphoric acid. Given that most of the uranium in phosphoric acid currently ends up in phosphate fertilizers, the extraction of uranium provides an added benefit, in that it reduces the potential for buildup of uranium in agricultural soils [278]. This section provides a summary of known best practices that may be adopted once uranium recovery from phosphoric acid is resumed in the near future.

Solvent extraction is currently regarded as the most highly proven and economic method of extracting uranium from phosphoric acid and will probably be the method of choice initially when production resumes. The ion exchange method is a promising alternative, but the technology is as yet unproven economically on a commercial scale. Continuing research into uranium recovery from phosphoric acid has resulted in a number of new, more powerful solvents as well as new ion exchange and membrane processes [279–281].

12.1. THE SOLVENT EXTRACTION PROCESS

12.1.1. Process description

12.1.1.1. Main process

In general, all successful uranium recovery processes based on solvent extraction consist of five steps:

- (i) Acid pretreatment;
- (ii) Primary solvent extraction;
- (iii) Raffinate post-treatment;
- (iv) Secondary solvent extraction;
- (v) Uranium refining.

There are also side stream operations such as residue treatment and strip acid preparation. The overall process is shown schematically in Fig. 65.

Acid pretreatment

Phosphoric acid is first cooled from 80°C to 30–50°C. This causes phosphogypsum impurities to come out of solution. These are usually removed by settling and returned to the phosphoric acid production process. Phosphogypsum also accumulates as scale in the heat exchangers and sometimes in the storage tanks. Activated carbon may be used to remove organic impurities from the phosphoric acid, after which the carbon is regenerated, typically with sodium hydroxide. The activated carbon absorbs radon which is not totally removed by the sodium hydroxide. Spent activated carbon is removed from the system as waste. If the uranium is to be extracted with a solvent that requires it to be in the U^{6+} state, the U^{4+} content of the phosphoric acid is oxidized to U^{6+} with air, oxygen, hydrogen peroxide, chlorine or nitric acid. If nitric acid is used, NO_x is emitted and usually has to be removed by a scrubber. If the uranium is to be extracted with a solvent that requires it to be in the U^{4+} state, the U^{6+} content of the phosphoric acid is reduced to U^{4+} by the addition of iron (scrap iron, iron balls or shredded iron) or ferrosilicon dust.

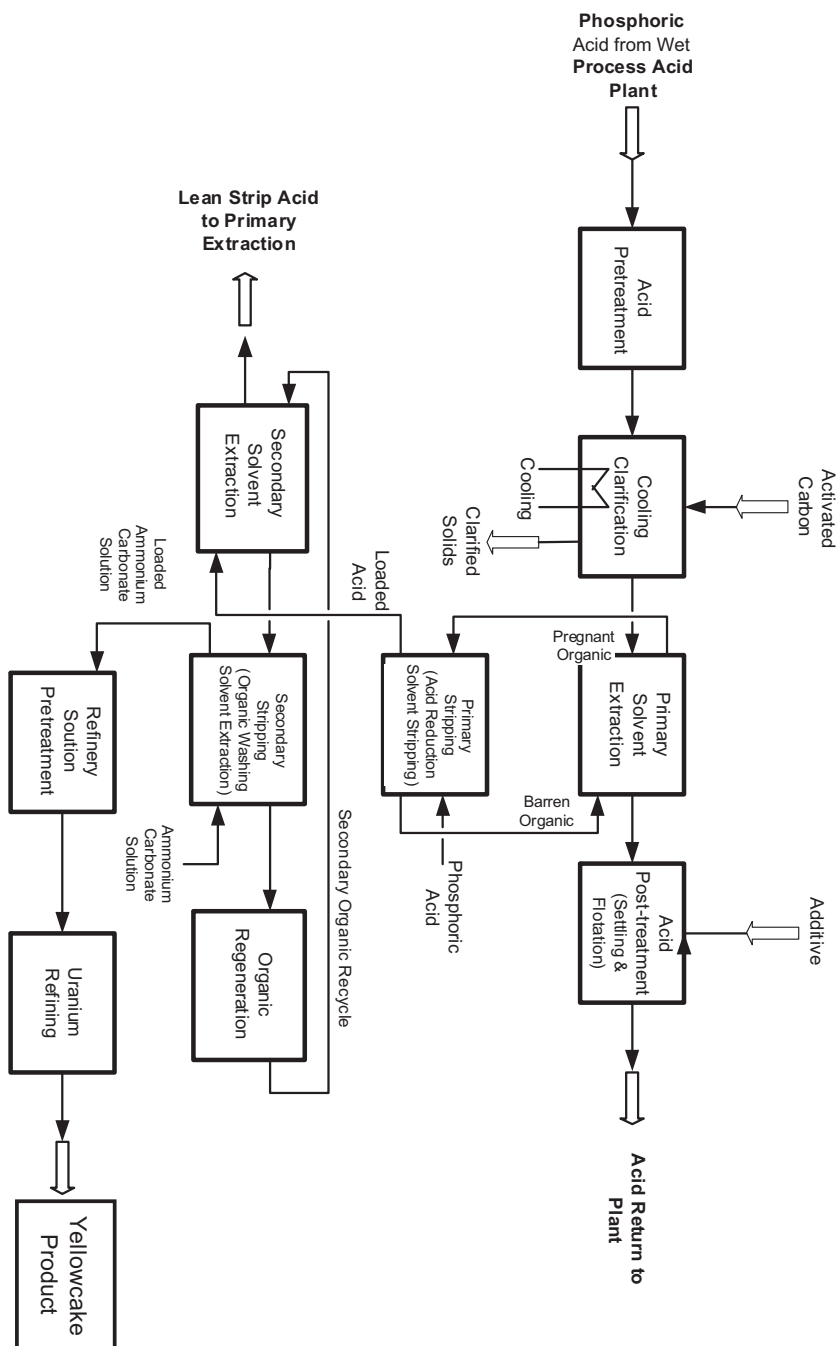


FIG. 65. Uranium recovery from phosphoric acid by solvent extraction.

Primary solvent extraction

The solvent is a mixture of an extractant and a diluent (typically a petroleum compound). Prior to the suspension of uranium extraction operations in the late 1990s, the most commonly used extractant was a synergistic mixture of di-(2-ethylhexyl) phosphoric acid (DEPA or D2EHPA) and tri-octylphosphine oxide (TOPO), which extracted uranium in the U^{6+} state. Octyl-phenylphosphoric acid (OPAP) and octyl-pyrophosphoric acid (OPPA), which extracted the uranium in the U^{4+} state, were also used. The pretreated phosphoric acid is contacted with the solvent in agitated mixer-settlers, in-line mixer-settlers or contacting columns. Typically, 3–6 stages of contact are used to remove 90–98% of the uranium from the acid. Depending on the solvent-to-acid ratio, the concentration of uranium attained in the solvent varies from 0.1 to 0.6 g/L, which is about 1–4 times the concentration in the original phosphoric acid. Stripping of the uranium from the solvent is accomplished by contacting the loaded solvent with phosphoric acid (27–50% P_2O_5). The strip acid is pretreated in one of two ways:

- (i) If the uranium has been extracted in the U^{6+} state, iron is first added to the strip acid to convert its entire uranium content to the U^{4+} state. Since the addition of iron can cause rapid and significant iron phosphate scaling, all critical process lines are duplicated so that one can be washed out while the other is in operation. Sulphuric acid may also be added to minimize the precipitation of iron phosphate compounds.
- (ii) If the uranium has been extracted in the U^{4+} state, an oxidizer is first added to the strip acid to convert its entire uranium content to the U^{6+} state. Traditionally, hydrogen peroxide has been used as an oxidizer, but oxygen, chlorine or nitric acid may also be used.

The concentration of uranium attained in the strip acid is typically 3–20 g/L.

Raffinate post-treatment

The phosphoric acid raffinate from the primary solvent extraction typically contains residual solvent at a concentration of about 100–500 ppm. Not only does this represent a loss of valuable solvent, but the diluent component can also cause damage to the rubber lined piping, evaporators and tanks that are downstream in the processing plant. The residual solvent is, therefore, removed in flotation cells. Using 5–10 such cells, the organic content of the raffinate can be reduced to less than 50 ppm.

Secondary solvent extraction

The uranium in the strip acid from the primary solvent extraction is oxidized to the U^{6+} state using oxygen, hydrogen peroxide or nitric acid. The uranium is extracted using, as an extractant, a synergistic combination of DEPA and TOPO in several countercurrent stages employing 3–6 mixer–settlers. The uranium concentration attained in the solvent is about 15–30 g/L. The loaded solvent is washed with water to remove any entrained phosphoric acid. Using ammonium carbonate solution in two stripping stages, almost the entire uranium content is then stripped from the solvent. Since the stripped solvent has an affinity for ammonia, it is subjected to two stages of sulphuric acid washing to remove any ammonia before being recycled back to the front end of the process. Otherwise, the ammonia would react with the iron and phosphate in the oxidized feed acid and cause iron ammonium phosphate to be precipitated. The uranium concentration attained in the ammonium carbonate solution is generally about 15–30 g/L.

Uranium refining

The uranium in the ammonium carbonate solution is precipitated as ammonium diuranate $((NH_4)_2U_2O_7)$, ammonium uranyl tricarbonate $((NH_4)_4UO_2(CO_3)_3)$ or uranyl peroxide $(UO_4 \cdot nH_2O)$. The precipitated uranium compound is known as ‘yellowcake’ because of its colour. The slurry is settled in a clarifier and extracted from the slurry feed either by centrifuging or filtration using pressure filters. The filtered cake is then sent to a dryer and optionally to a calciner. The calcined product contains more than 95% U_3O_8 together with small amounts of UO_2 and UO_3 . It is usually drummed and sent by truck to a conversion plant where it is converted to UF_6 for enrichment. A typical truck shipment consists of about 18 t of yellowcake packaged in 40–50 drums, each containing 350–450 kg of product. Drums awaiting shipment are kept in a temporary storage area at the extraction plant accommodating up to 100–150 drums, thus providing sufficient capacity to cater for interruptions in trucking schedules. In areas of the plant where dry yellowcake is handled, the dust levels in the air are carefully controlled by ventilation, air scrubbers and HEPA filters.

12.1.1.2. Management of residues

The spent sodium hydroxide solution from the acid pretreatment step is sent to the acidic process water pond. The spent carbon may have a significant radioactivity content and its handling and disposal is, therefore, controlled

appropriately. During the primary solvent extraction process, various residues are generated:

- (a) An interfacial layer is formed, consisting of an emulsion of 1–5% solids in a similar volume of acid and solvent. The solids are insoluble in both acid and solvent. The layer is removed by suction pumping. While most of the acid and solvent can be removed from this residue using a pre-coat drum filter, chemical treatment or centrifuging, it is still one of the main causes of solvent loss. The formation of this residue is influenced by the effectiveness of the acid pretreatment step. The residue is disposed of either in the phosphogypsum stack or by burial on-site.
- (b) Solid residues may be generated in the extraction mixer–settlers. If there is significant cooling of the acid, phosphogypsum and fluosilicates will precipitate. While some of these solids will end up in the interfacial layer, most will collect in the bottom of the settlers, which, therefore, have to be washed out periodically. About 20–40% of the content of the solids consists of acid. The solids, therefore, have a uranium concentration of up to 0.1 g/L. They are disposed of either in the phosphogypsum stack or by burial on-site.
- (c) Solids are generated in the strip system when Fe^{2+} is oxidized to Fe^{3+} by the reduction of U^{6+} . This Fe^{3+} reacts with the phosphoric acid and any monovalent cations present to form iron phosphate compounded with ammonium, sodium or potassium. These solids generally end up at the bottom of the settler, but some may become entrained in the interfacial layer. The solids are removed periodically by washing out the solids with water or removing them manually. About 20–40% of the content of the solids consists of acid. The solids, therefore, have a uranium concentration of up to 8 g/L. They are disposed of either in the phosphogypsum stack or by burial on-site.

All the above disposal methods adopted in the past are unlikely to be practised in a future situation mainly owing to technological and regulatory improvements.

In the secondary solvent extraction, since the iron in the feed acid has been oxidized, there is significant precipitation of iron phosphate compounded with ammonium, sodium or potassium. These solids rapidly fill the settlers and must be removed as frequently as every few days. About 20–40% of the content of the solids consists of acid. The solids, therefore, have a uranium concentration of up to 8 g/L.

Throughout the extraction plant, there is a general tendency for uranium rich residues to accumulate on the surfaces of process equipment such as pipes, sumps and drains. Examples of such buildup are shown in Fig. 66.



FIG. 66. Buildup of uranium rich residues within a solvent extraction plant.

12.1.2. Radionuclide activity concentrations

Pure uranium oxide (U_3O_8) contains ^{238}U and ^{234}U each at activity concentrations of 12 347 Bq/g and ^{235}U at an activity concentration of 568 Bq/g. It follows from the very purpose of the solvent extraction process, therefore, that many of the process materials and residues involved are likely to contain these uranium isotopes at very high activity concentrations. A summary of ^{238}U activity concentrations in the various process materials and residues associated with the solvent extraction process is given in Table 40 [282]. The dried yellowcake product has a ^{238}U activity concentration of the order of 10 000 Bq/g.

Radionuclides other than ^{238}U and ^{234}U , especially the remaining decay progeny of ^{238}U , are present in significant concentrations in materials associated with the acid pretreatment step. Here, residues consisting essentially of phosphogypsum and having a radionuclide composition similar to that of bulk phosphogypsum are precipitated as solid particles or deposited as scale. The spent activated carbon removed from the acid pretreatment step may have a significant radioactivity content resulting from the absorption of radon. From the point at which uranium is extracted from the phosphoric acid in the primary solvent extraction, the activity concentrations of radionuclides other than ^{238}U , ^{234}U and ^{235}U can be expected to be very low in relative terms. In absolute terms, however, such activity concentrations may still be significant. For instance, the activity concentration of ^{226}Ra in 65% grade yellowcake product is about 7.4 Bq/g.

TABLE 40. URANIUM-238 ACTIVITY CONCENTRATIONS IN PROCESS MATERIALS AND RESIDUES ASSOCIATED WITH THE SOLVENT EXTRACTION PROCESS

Extraction process	Activity concentration (Bq/L) ^a
<i>Primary solvent extraction:</i>	
Loaded solvent	1300–7900
Loaded strip acid	40 000–260 000
Interfacial residue and, where used, filter pre-coat	Similar to or less than that in the incoming phosphoric acid ^b
Solids from extraction mixer–settlers	Up to 1300
Solids from strip system	Up to 100 000
<i>Secondary solvent extraction:</i>	
Loaded solvent	190 000–380 000
Loaded ammonium carbonate solution	190 000–380 000
Solids from mixer–settlers	Up to 100 000

^a For solids, the activity concentration is given as becquerels per kilogram.

^b For phosphoric acid produced from sedimentary rock in Florida, USA, the range of U-238 concentrations is 3500–5200 Bq/L.

12.1.3. Occupational exposure

12.1.3.1. Exposure pathways and exposure levels

Solvent extraction of uranium from phosphoric acid is not a labour intensive process. The number of workers employed per shift in an extraction plant is between 4 and 20, or even fewer in a plant with computerized process control systems. The potential for external gamma exposure is moderate because the workers tend to spend only short periods in areas of high dose rates and the concentrations of gamma emitting radionuclides such as radium and its progeny are relatively low. Furthermore, exposures to the yellowcake product are moderated by the shielding provided by centrifuge enclosures and the drums within which the product is packaged. Nevertheless, exposure to drums of yellowcake can become significant in the temporary storage area because of the number of drums stored. The dose rate on contact with a drum of yellowcake may reach 100 µSv/h, depending on the concentrations of ²³⁸U decay progeny. The main potential exposure pathway is the inhalation of airborne dust, particularly for workers engaged in yellowcake drying and packaging activities. Ingestion of

uranium as a result of contamination of skin and clothing is a concern, but more because of the chemical toxicity of uranium rather than its radiological effects.

12.1.3.2. Monitoring techniques for workers

External exposure is monitored using personal dosimeters (LiF TLDs or $\text{Al}_2\text{O}_3\text{:C}$ OSLDs) worn on the chest and extremity dosimeters worn on the fingers. Monitoring of dust activity concentrations in the air, particularly in areas where yellowcake is handled, is carried out using stationary air sampling or personal air sampling. Workers who routinely handle yellowcake may be monitored using urine analysis, typically on a quarterly basis, to confirm that intakes of uranium continue to be low. The external surfaces of drums of yellowcake are checked with surface contamination monitors before shipping.

12.1.3.3. Effective dose

Although published data on annual effective doses received by workers in past operations are not available, reports suggest that such doses are usually not more than a few millisieverts and well below the occupational dose limit of 20 mSv.

12.1.3.4. Measures to reduce doses

Spillages can lead to workers being unexpectedly exposed to material with high activity concentrations. For instance, if the loaded solvent from secondary solvent extraction is spilled on the floor area surrounding the process equipment (typically a concrete pad), evaporation of the solvent can cause the uranium concentration to rise far above the normal level of 15–30 g/L. If all the solvent evaporates, the uranium content of the residue can be as high as 30%. At this level, the activity concentrations of ^{238}U and ^{234}U will each be almost 4×10^6 Bq/L. Such exposures can be avoided if care is taken to prevent such spillages and, if they do occur, to keep the area around the solvent extraction system flushed with water to prevent the buildup of high activity residues.

The use of thick, concrete walls for the construction of the yellowcake storage area has been found to provide effective shielding from the high dose rates in that area. In this way, the external exposure of workers on the other side of the wall is reduced to levels where no special precautions need be taken against external exposure.

Other measures that are known to be effective in reducing occupational exposure in solvent extraction plants include:

- (a) The adoption and enforcement of procedures to ensure that equipment, especially air filtration equipment, is properly maintained;
- (b) The adoption and enforcement of good, general housekeeping measures, including the removal of settled dust and of sediments that build up on equipment such as structural steel, pipes and drains (see Fig. 66), so that the levels of contamination in the plant remain under adequate control;
- (c) The use of smooth, hard finishes, such as epoxy coatings on floors and walls, to improve the effectiveness of routine cleaning and to facilitate the cleanup of spillages;
- (d) The provision of suitable bounded areas (berms and sumps) around process equipment having the greatest potential for major spillage;
- (e) Maintenance of high levels of worker training and awareness;
- (f) The provision of protective clothing, footwear barriers and decontamination facilities;
- (g) The provision of respiratory protective equipment for certain tasks such as the changing of air filters, where engineering controls and administrative measures alone are not sufficient to control worker exposures adequately;
- (h) Restrictions on eating, drinking and smoking in certain areas;
- (i) Ensuring the effectiveness of administrative controls, such as the designation of controlled and supervised areas and the maintenance of strict access control.

12.1.4. Public exposure

There are normally no significant exposure pathways to members of the public from solvent extraction facilities. Liquid effluents are not discharged without adequate treatment. Gaseous discharges from ventilation systems are controlled by scrubbers and HEPA filters. Most of the radioactive residues generated by the process are recycled back to the process or, where disposed of as waste, are buried on the site, either in the phosphogypsum stack or nearby. The traditional practice of on-site burial in or next to the phosphogypsum stack may have to change in future to meet the changing regulatory requirements in respect of waste management practices. If future phosphogypsum stacks are no longer to be treated as disposal sites but, instead, as temporary holding areas pending future use of the phosphogypsum, then radioactive waste from the solvent extraction process will have to be kept separate and transported off the site to a suitable radioactive waste disposal facility.

12.2. OTHER PROCESSES FOR THE EXTRACTION OF URANIUM

12.2.1. Ion exchange extraction

Ion exchange is a potentially attractive process for uranium recovery from phosphoric acid, presenting both challenges and opportunities [283, 284]. Compared with the solvent extraction process, the ion exchange process requires fewer pretreatment and post-treatment steps and offers potential economic advantages. The technology is, as yet, unproven on a commercial scale, but pilot testing, which is well advanced, has indicated several provisional but nonetheless positive conclusions. Compared with the solvent extraction process, the ion exchange process:

- (a) Is potentially advantageous from an environmental point of view, because it avoids the generation of (radioactive) solvent extraction residue;
- (b) Is better suited for feed phosphoric acid with uranium concentrations of less than 300 mg/L;
- (c) Tends to have lower capital and operating costs for low uranium concentrations in the feed acid;
- (d) May be tolerant of higher process temperatures (up to 80°C), a potentially significant cost saving as compared with solvent extraction, which may require the acid feed to be reheated on return to the phosphoric acid plant;
- (e) May be more tolerant of organic acids in the feed acid;
- (f) Eliminates the requirement for post-treatment of phosphoric acid raffinate;
- (g) When used as a fluidized bed system, is tolerant of solids in the feed acid, implying a reduced need for clarification in pretreatment steps.

12.2.2. Solid membrane extraction

Uranium can be removed directly from phosphoric acid in a single step using porous membranes. This process yields very pure phosphoric acid and efficient uranium recovery in a single stage. However, the recovered uranium is a supersaturated concentrate containing chemical impurities that have also been removed from the acid. These impurities must be separated and removed as a waste stream. The membranes themselves are likely to become repeatedly clogged and quickly worn out, necessitating vigilant, well-trained operators and an effective, well-supervised maintenance and renewal regime. The disposal of the impurities removed from the process and of the spent membranes may have radiological implications.

12.2.3. Liquid membrane extraction

Liquid membrane extraction is based on an emulsion containing both a liquid membrane extractant and a stripping solution. The extractant could be one of those used for solvent extraction, such as OPAP or DEPA–TOPO. Uranium is removed from the surfactant-stabilized membrane in an aqueous stripping phase. Very high uranium recoveries are achieved. A coalescent breaks down the uranium laden emulsion for recovery.

12.3. REGULATORY CONSIDERATIONS

Owing to the very high activity concentrations of uranium isotopes and other radionuclides in the yellowcake product and most of the intermediate process materials and residues, the extraction of uranium from phosphoric acid, regardless of the process used, is unquestionably regulated as a practice. Experience with extraction plants operated in the past has shown that workers received committed effective doses that under normal circumstances did not exceed a few millisieverts per year. There are no significant exposure pathways to members of the public. However, a formal (and effective) radiation protection programme, which includes a comprehensive monitoring programme, is the only way to ensure that workers do not receive much higher doses. Further details on the content of such a programme are given in Ref. [4]. In addition, the disposal of the radioactive waste generated by the solvent extraction process has to be carried out under controlled conditions. Consequently, the most appropriate regulatory option is a requirement for an authorization in the form of a registration or licence, the choice depending very much on the national approach. In many countries, the fact that uranium extraction is part of the front end of the nuclear fuel cycle necessitates that the authorization be in the form of a licence.

Owing to the high activity concentrations, the transport of yellowcake off the site and of any radioactive waste destined for off-site disposal falls firmly within the scope of the Transport Regulations.

13. PRODUCTION OF ELEMENTAL PHOSPHORUS BY THERMAL PROCESSING OF PHOSPHATE ROCK

Thermal processing of phosphate rock to produce elemental phosphorus using the so-called electric furnace method was developed in the USA from 1933 onwards by the Tennessee Valley Authority (TVA) and was widely used to produce phosphoric acid during the period 1934–1977 in countries such as Canada, China, Germany, Kazakhstan, Netherlands and the USA [45].

In the past, phosphate rock was also thermally processed using the so-called blast furnace method. This process, which was originally used during the period 1929–1939 [45], had the advantage of being able to make use of low grade phosphate rock, provided that the main impurity was silica, with both iron oxide and alumina causing less difficulty in production than was the case for the wet process. In the late 1940s, the TVA investigated further improvements to the blast furnace process [285]. An attempt to revive the process in the late 1960s foundered on the high cost of coke [286], leaving the electric furnace method as the only method in use.

The thermal process has been used mainly for the production of high purity ('furnace grade') phosphoric acid, which is a constituent of products such as industrial chemicals, insecticides, detergents, food additives and feeds. Although the process still plays an important role in phosphoric acid production worldwide, its use has declined from past levels. At the end of 2001, one of the last two elemental phosphorus production facilities in the USA was shut down, leaving only one facility (at Soda Springs, Idaho) in operation in that country. Another facility continues to operate at Vlissingen, Netherlands. More recently, significant increases in the price of sulphur (a source of sulphuric acid used extensively in the wet process) have created conditions for a resurgence of interest in the thermal process. In China, for example, the nature of energy production, largely based on hydroelectric generation at a local level, has supplied inexpensive power to phosphoric acid plants for many decades. Since thermal acid production is very energy intensive, this advantage has been decisive in retaining a large thermal phosphorus production capacity in China, despite the fact that more recent joint ventures with Western companies have now brought wet acid production, as well as MAP and DAP production, to China on a large scale.

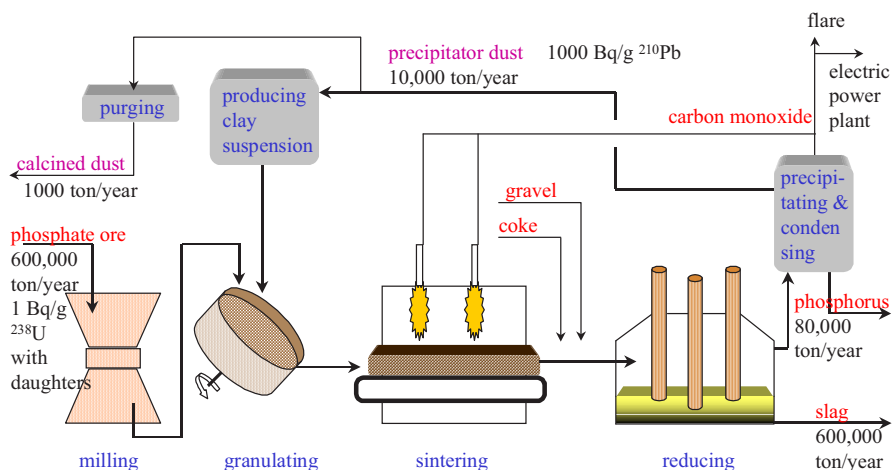


FIG. 67. Schematic representation of the thermal phosphorus process used by TIBV (from Ref. [287]). The numerical values are representative only and may vary considerably, depending on the characteristics of the phosphate rock feedstock.

13.1. PROCESS DESCRIPTION

13.1.1. Main process

Sintered pellets produced from finely powdered phosphate rock are fed into an electric arc furnace together with gravel and coke. The reduction of the phosphate produces elemental phosphorus along with calcium silicate slag, carbon monoxide and calcium fluoride according to the following chemical reaction:



A schematic representation of the process used at a plant operated by Thermphos International BV (TIBV) in the Netherlands (formerly part of Hoechst Holland NV) is shown in Fig. 67. This plant produces 80 000 t of elemental phosphorus, 600 000 t of calcium silicate slag and 4000 t of ferrophosphorus annually. The phosphate ore is first milled to a fine powder, which is then fed to a rotating granulator disc together with a binder consisting of a suspension of clay in water together with recycled precipitator dust. The rotation of the disc results in the formation of pellets. The pellets are fed to the front end of a slowly rotating sintering grate. They pass through a drying zone maintained at a temperature of up to 300°C and are then sintered to hard spheres

under two large burners at a temperature of about 800°C. The pellets then pass through a cooling zone. The heat released from the pellets is directed to the drying zone. The pellets are then conveyed to an intermediate storage facility where they are stored in large silos in readiness for feeding to the electric furnaces. In sintering plants operating in other countries, the sintering process may differ in that the phosphate rock is not milled and a higher sintering temperature is used.

The sintered phosphate feedstock material is fed into an electric arc furnace together with the gravel and coke. The chemical reaction in which phosphate ore is reduced to elemental phosphorus takes place at temperatures exceeding 1500°C. The elemental phosphorus leaves the furnace as a gas, together with the carbon monoxide formed during the reaction. After removal of entrained dust, the gases are cooled, causing the phosphorus to condense to a stream of liquid phosphorus.

Production of phosphoric acid from elemental phosphorus is reasonably straightforward. Liquid elemental phosphorus is burned in air and the resulting P_2O_5 is then hydrated to create furnace grade phosphoric acid. The overall reaction may be characterized as:



13.1.2. Management of residues

The calcium silicate slag produced during the process flows continuously from the furnace. Trace amounts of iron are also reduced in the furnace. These form a separate slag, ferrophosphorus, containing approximately 75% iron, 25% phosphorus and small amounts of other metals. The calcium silicate slag is a stone-like by-product with applications as a construction material for roads, dykes and possibly dwellings. It is a good substitute for gravel, the mining of which can have undesirable environmental consequences through the formation of gravel pits. When used in a road bed, especially when used together with steel slag, its angular structure imparts greater resistance to subsidence.

At the high temperatures prevailing in the furnace, volatile inorganic substances, metals and radionuclides evaporate and condense on dust particles. The dust is trapped in electrostatic precipitators. In the TIBV plant, about 10 000 t of precipitator dust is produced annually, most of which is recycled back to the sintering plant. It is fed to slurry tanks where it is mixed with water and pumped to the 'slurry station' for reuse as a component of the binding suspension used for pelletizing the phosphate powder. When the volatile inorganic substances, metals and radionuclides contained within the precipitator dust reach the furnace for the second time, they evaporate again. In this way, these substances become enriched

in the so-called precipitator dust cycle. High concentrations of volatile inorganic matter and metals cause instability in the operation of the furnaces. To control the concentration, 500–1000 t of precipitator dust are purged from the system annually by diverting the dust stream to a purge unit housed in the slurry station. The purge unit consists of a high pressure filter and a rotating calcining kiln where the pressed, lumped precipitator dust is calcined at temperatures of 400–500°C before being removed as waste. The recycling of precipitator dust in this manner reduces the amount of solid waste requiring disposal, but increases the emissions of radionuclides to the atmosphere. Modifications to the precipitator dust recycling process have since been made to reduce these radionuclide emissions [288]. In plants in other countries, it has been more common in the past for the precipitator dust to be disposed of rather than recycled back to the process.

Calcined precipitator dust produced in past operations at the TIBV plant at a rate of 500–1000 t/a is stored on-site. Calcined dust from current operations is being stored at the centralized COVRA radioactive waste storage facility. Storage allows the ^{210}Pb to decay sufficiently for the material to be disposed of in a landfill facility after immobilization in cement [289]. For instance, after 150 years, the ^{210}Pb activity concentration will have fallen from 1000 Bq/g to 10 Bq/g. The material at COVRA is stored in containers fitted with plastic linings and stacked in a purpose-built storage building. To avoid taking up excessive space in the storage building, immobilization in cement will be carried out only after the decay storage period has elapsed.

13.2. RADIONUCLIDE ACTIVITY CONCENTRATIONS

During the sintering process, ^{210}Po , which has a half-life of 138 d, volatilizes and escapes from the feedstock material. It passes through the scrubbers that wash the sinter gases and is emitted to the atmosphere. Most of the ^{210}Pb , which is less volatile than ^{210}Po , remains in the sintered feedstock.

In the furnace, the radionuclides above ^{222}Rn in the ^{238}U decay chain (see Appendix I) remain in the melt and become part of the calcium silicate slag. Of the radionuclides escaping from the melt, the two most important in terms of gamma dose (^{214}Pb and ^{214}Bi) grow back into the slag after about two weeks. Since approximately one tonne of slag is formed per tonne of phosphate rock feedstock, the activity concentrations of ^{238}U , ^{214}Pb and ^{214}Bi in the slag are similar to those in the feedstock (about 1 Bq/g). The ^{222}Rn escaping from the melt leaves the furnace along with the carbon monoxide. Only those radionuclides below ^{222}Rn in the ^{238}U decay chain end up in the precipitator dust. Consequently, the ^{238}U activity concentration in the precipitator dust is low, with a maximum

value of about 1 Bq/g. The behaviour of the radionuclides in the precipitator dust can be summarized as follows:

- (a) The short lived progeny of radon (^{218}Po , ^{214}Pb , ^{214}Bi and ^{214}Po) decay within a few hours.
- (b) In the TIBV process, the relatively long lived ^{210}Pb (half-life of 22 a) builds up in the precipitator dust during the recycling process to an activity concentration of about 1000 Bq/g, representing a thousandfold enrichment of this radionuclide. Owing to the loss of ^{210}Po during the sintering of the pellets, the activity concentration of ^{210}Po in the precipitator dust is initially only about 60 Bq/g, considerably lower than the activity concentration of ^{210}Pb . The half-lives of ^{210}Bi and ^{210}Po (progeny of ^{210}Pb) are 5 and 138 d, respectively, and after about four half-life periods, these progeny are again present in the precipitator dust at nearly the same activity concentration as that of the parent radionuclide, ^{210}Pb .

Very little radioactivity migrates to the elemental phosphorus product or to the ferrophosphorus slag. The phosphorus contains ^{226}Ra at an activity concentration of 0.03 Bq/g, while the ferrophosphorus contains ^{238}U series radionuclides each at an activity concentration of 0.03 Bq/g.

13.3. OCCUPATIONAL EXPOSURE

13.3.1. Exposure pathways

Phosphorus plant workers are exposed to airborne dust originating from the phosphate rock, but since the activity concentrations are low, the exposure levels are not significant. In the case of the TIBV plant, where the recycling of precipitator dust is carried out, the activity concentrations of ^{210}Pb and ^{210}Po in the dust are approximately 1000 times higher than in the phosphate rock. This then becomes the main source of exposure of plant workers.

13.3.2. Exposure of plant workers

13.3.2.1. Monitoring techniques

This section describes the monitoring techniques used for workers at the TIBV plant. To determine the intakes of radionuclides by workers, TIBV makes measurements using personal air sampling equipment comprising a battery powered air pump connected by a flexible tube to a filter located in a filter holder [287].

During the period 1998–2003, TIBV sampled the inhalable dust fraction using an IOM sampling cassette (see Fig. 3). Since 2004, a thoracic sampler has been used instead (see Fig. 4) [290], in order to minimize dose assessment errors (see Section 3.3.2). The equipment is carried by the worker in such a way that a continuous sample of the air surrounding the worker passes through the filter. The dust is separated from the air and collected on the filter. The worker carries the personal air sampler for the working shift of 8 h.

Alpha and beta activities on the filter are measured using a proportional counter capable of discriminating between alpha and beta radiations. The achievement of the necessary statistical accuracy requires a counting time of 5 d, necessitating the use of a 10 channel counter. The activity of ^{210}Pb on the filter cannot be measured directly because the beta emission from this radionuclide is very weak. It is determined, instead, from the beta emission from ^{210}Bi , which has a maximum energy of 1.16 MeV. To ensure that ^{210}Bi reaches radioactive equilibrium with its parent ^{210}Pb , it is necessary to retain the filter for three weeks before carrying out the measurement. The alpha emission from ^{210}Po has an energy of 5.3 MeV, allowing the activity of this radionuclide to be measured directly.

The worker's radionuclide intake is determined from the count rates obtained from the filter, the rate of air flow through the filter, the worker's breathing rate (usually taken as $1.2 \text{ m}^3/\text{h}$) and the exposure time (typically 8 h). For those work functions associated with the highest intakes and a wide confidence interval, the frequency of measurement is increased in order to narrow the confidence interval and thus obtain a more accurate dose assessment.

Dissolution tests conducted at TIBV indicate that the slowest lung absorption type (S) is the most appropriate for dose calculation purposes. Assuming this lung absorption type, the committed effective doses per unit intake of radionuclide activity have been determined for ^{210}Pb and ^{210}Po as functions of AMAD and GSD. The results are shown in Figs 68 and 69. Since, for AMADs of $0.5\text{--}5 \mu\text{m}$, the dose coefficients remain within a relatively small range, TIBV uses dose coefficients representative of this range, namely 5.8 and $4.2 \mu\text{Sv/Bq}$ for ^{210}Pb and ^{210}Po , respectively.

TIBV has carried out a dust characterization using a cascade impactor to determine the activity distribution as a function of particle size. The results indicate that there is considerable activity associated with particles having an AMAD greater than $0.5\text{--}5 \mu\text{m}$, especially where workers produce the dust themselves during cleaning work. Under such circumstances, a considerable part of the activity intake is believed to originate from dust particles with AMADs of $5\text{--}10 \mu\text{m}$ and greater. The implication for a worker involved in cleaning work with freshly produced airborne dust is that the dose determined on the basis of an AMAD of $0.5\text{--}5 \mu\text{m}$ will be overestimated because of the lower dose coefficients associated with these larger particles.

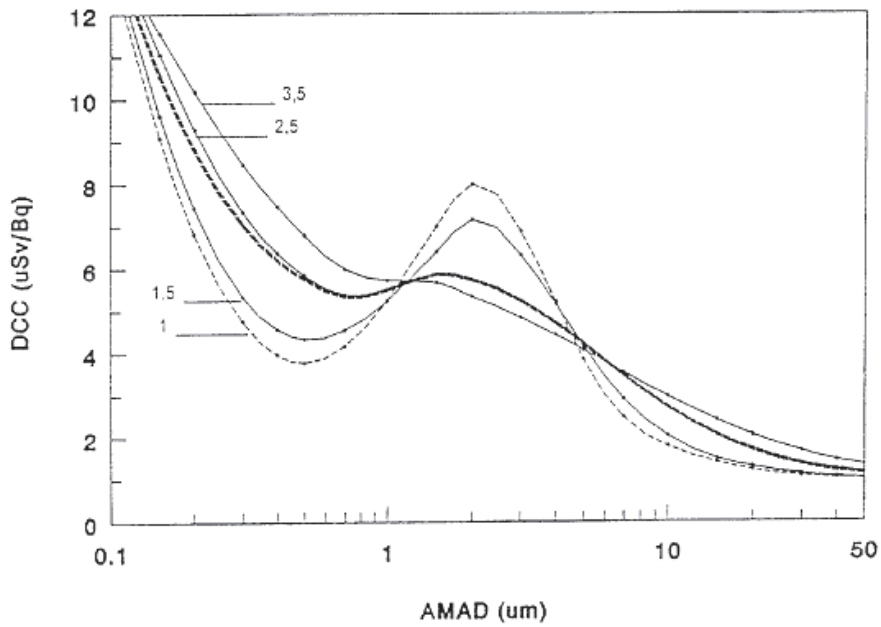


FIG. 68. Dose per unit intake for ^{210}Pb , lung absorption type S, as a function of AMAD and GSD.

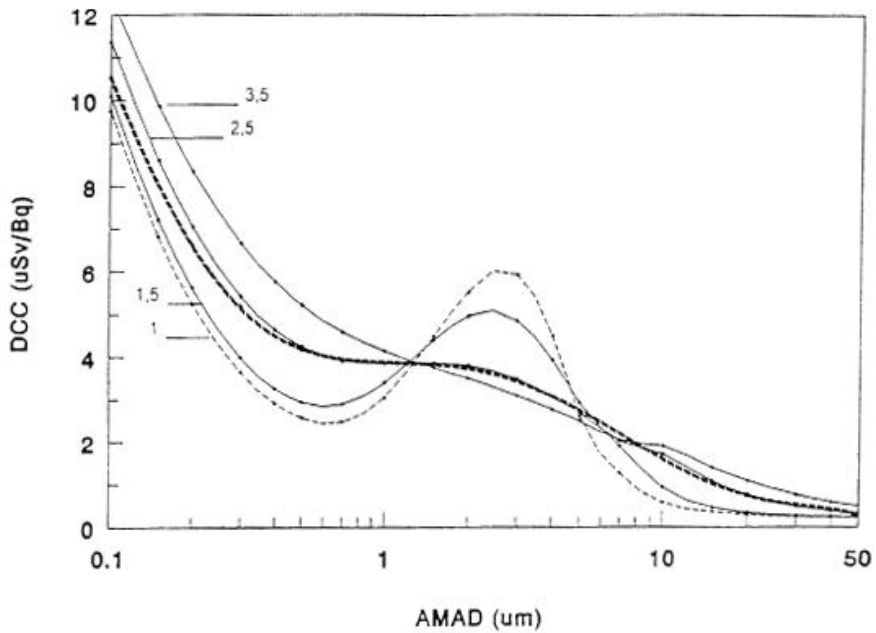


FIG. 69. Dose per unit intake for ^{210}Po , lung absorption type S, as a function of AMAD and GSD.

13.3.2.2. Effective dose

To simplify the dose calculation, it can be assumed that all the inhaled alpha activity originates from ^{210}Po and all the inhaled beta activity originates from ^{210}Pb . The results of the dose assessments carried out since 2004 at the TIBV plant using thoracic sampling devices [288] are given in Table 41. The average

TABLE 41. DOSES RECEIVED BY WORKERS AT THE TIBV THERMAL PHOSPHORUS PLANT [288]

Worker	Annual committed effective dose (mSv)			Contribution of Pb-210 to dose (%) ^a	Average dose for 1998–2003 assessed using ‘inhalable dust’ samplers (mSv) (for comparison)
	Average	Standard deviation	90% confidence interval		
<i>Sintering plant:</i>					
Indoor operator	0.67	0.57	0.48–0.86	64	1.63
Granulating operator	0.47	0.31	0.31–0.63	52	1.03
Slurry operator	0.48	0.42	0.28–0.68	60	0.66
Cleaning operator	0.74	0.45	0.61–0.87	53	2.17
Overall	0.57	0.39	0.51–0.63	54	1.31
<i>Phosphorus plant:</i>					
Filtration	0.23	0.07	0.18–0.28	63	0.39
Condensation	0.28	0.12	0.21–0.35	58	0.52
Electrode welder	0.33	0.16	0.25–0.41	66	0.63
Daytime operator	0.29	0.12	0.19–0.39	72	0.95
Furnace feed	0.44	0.42	0.29–0.59	67	0.72
Slag operator	0.34	0.21	0.17–0.51	59	0.56
Slurry operator	0.41	0.23	0.32–0.50	70	0.64
Cleaning operator	0.48	0.27	0.36–0.60	72	1.59
Overall	0.33	0.19	0.30–0.36	70	0.90
Supervisors	0.26	0.17	0.22–0.30	65 ^b , 73 ^c	0.65 ^b , 1.37 ^c
Overall (both plants)	0.43	0.35	0.38–0.48	61	1.09

^a Obtained from 1998–2003 measurements.

^b Shift supervisor.

^c Assistant supervisor.

annual effective doses are well below 1 mSv throughout the plant, with an overall average of 0.43 mSv. The highest dose (upper 90% confidence limit) is 0.87 mSv, received by the cleaning operator in the sintering plant. The contribution of ^{210}Pb to the total dose is about 50–70%, with ^{210}Po accounting for the rest. Also shown in Table 41 are the average doses assessed during 1998–2003 by sampling the inhalable fraction using IOM cassettes. A comparison of the two sets of results gives an indication of the amount by which the dose was overestimated in the past as a result of using an AMAD range of 0.5–5 μm , when a substantial fraction of the activity was associated with particles with AMADs greater than 5 μm (see Section 13.3.2.1). Overall, the doses were overestimated by a factor of 2.5.

The variation in assessed doses is large because work activities can differ from day to day and the concentrations of radionuclides in the air fluctuate widely. In earlier monitoring programmes at TIBV, it was found that the dose assessed over the standard one day measuring period varied from zero up to five times the average daily value [287]. The achievement of small confidence intervals for every work function would require a prohibitively large number of measurements being taken. For all the functions together within one plant, however, the confidence interval was considered acceptable.

The dose variations depend on the process (which is predetermined) and on the specific working conditions and work practices that affect the exposure of the worker (which are less easy to predict). The following examples were found at the TIBV plant:

- (a) Two workers carried out the same cleaning work on the same floor. After the work was completed, the first worker was covered in dust while the other was clean. The first worker used a broom for certain cleaning activities whereas the other used only the prescribed vacuum cleaner. Both operators inhaled the same ‘background’ air. The committed effective dose assessed for the first worker was 0.02 mSv over just that one working shift, while the dose for the second worker was almost zero. This demonstrated that the background air was essentially free of radionuclides and that the dose received was influenced almost entirely by the working activities and especially the way in which they were carried out.
- (b) Some workers, such as electrode welders, work in an environment in which there is no contamination of surrounding surfaces and, thus, no possibility of receiving a dose from the resuspension of dust. It was demonstrated, however, that the air in such a workplace was contaminated by the activities necessary to remove slag (into slag beds situated immediately next to the furnace building) and ferrophosphorus from the furnace.
- (c) Large surface areas of some workplaces were contaminated by dry precipitator dust containing ^{210}Pb and its progeny at an activity

concentration of 1000 Bq/g. This contamination did not always lead to a dose; daily monitoring of workers in these areas often gave an assessed dose of zero. Simply walking through the contaminated area did not necessarily lead to inhalation of the dust because of the distance between the resuspension point (the feet) and the inhalation point (the nose and mouth). However, if work had been carried out at a fixed location in that area, the resuspended particles could have been inhaled and would have led to an effective dose of 0.04 mSv committed over the course of just one working shift. On one occasion, a compressed air hose broke loose from its connection and dust was blown from the floor over a period of several minutes. The exposure measured over the full working shift corresponded to a dose of 0.12 mSv committed in just that one shift.

- (d) Measurements showed that it was possible to create concentrations of dust that, if inhaled, would result in an effective dose of up to 1 mSv being committed in a 1 h period if highly contaminated parts of an installation were subjected to various mechanical procedures to remove surface contamination, thereby causing the resuspension of contaminant particles into the air. Contamination levels of several hundred becquerels per square centimetre have been measured on internal surfaces of process equipment. Under normal circumstances, workers are not exposed to these high levels of contamination but, when the installation is opened for maintenance or repair, measures have to be taken to prevent large inhalation doses from being received.

13.3.2.3. Measures to reduce doses

At the TIBV plant, by taking more measurements at the same time at different places in a working area and comparing them with earlier measurements, taking the working and process conditions into account, it has been possible to determine the pathways by which the radionuclides liberated from the process reached the workers involved. This has allowed dose reduction measures to be identified. An aerosol monitor giving 3 h average measurements has been used to study the fluctuations in concentration of alpha and beta emitting radionuclides in air. With this device, it is possible to identify sources of dust responsible for enhancing air concentrations.

Measures taken at the TIBV plant to reduce doses from inhalation of dust include the following:

- (a) Conduct of large scale continuous cleaning operations;
- (b) Renewal and coating of floor surfaces to enable them to be decontaminated more easily;



FIG. 70. Half-mask respirator.

- (c) Prevention of contamination by the installation of new measuring instruments and automation to monitor and control the process;
- (d) Improved ventilation at the ferrophosphorus outlet of the furnaces;
- (e) Relocation of the slag beds away from the furnace building;
- (f) Installation of central vacuum cleaning systems to avoid the need to open and empty mobile vacuum cleaners.

In addition, safety procedures attempt to minimize the possibility of higher exposures. If a vessel, sintering oven or furnace has to be opened and workers have to enter, the surface contamination levels are measured first. If the contamination level is less than 0.25 Bq/cm^2 , workers may enter without protective equipment. If the contamination level is $0.25\text{--}10 \text{ Bq/cm}^2$, a half-mask respirator with an assigned protection factor of 20 is worn (see Fig. 70). If the contamination level exceeds 10 Bq/cm^2 , a full face mask respirator with remote air supply is worn (see Fig. 71). These criteria have been derived conservatively from the results of measurement programmes, but are intended to apply only to inspection work or to other activities that do not produce significant amounts of dust. For activities producing dust, a full face mask respirator with remote air supply is worn, irrespective of the surface contamination level.



FIG. 71. Full face mask respirator with remote air supply.

13.4. PUBLIC EXPOSURE

13.4.1. Discharges from the plant

13.4.1.1. Inhalation exposure

During thermal phosphorus production, the radionuclides above ^{222}Rn in the ^{238}U decay series remain in the slag and are, therefore, not emitted to the atmosphere. Radon escapes from the melt and its short lived progeny ^{218}Po , ^{214}Pb , ^{214}Bi and ^{214}Po decay within a few hours. Exposures of members of the public to radon and its short lived progeny, as well as to ^{210}Bi , are negligible [291]. The only radionuclides of interest from a public exposure point of view are ^{210}Po and ^{210}Pb . The relatively volatile ^{210}Po escapes from the pellets during sintering and most of it is emitted to the atmosphere, despite intensive scrubbing of the exhaust gases. Although ^{210}Pb is less volatile, at the TIBV plant, the recycling of the ^{210}Pb rich precipitator dust can result in an annual emission of this radionuclide relative to ^{210}Po of up to about 50%, depending on the type of ore used in the process.

Table 42 shows details for the two year period 1994–1995, when the majority of the ore was obtained from Florida, USA [292, 293], and for the two year period 2002–2003, when the majority of the ore was obtained from Mediterranean and Middle Eastern countries [294, 295]. During the former period, the emission of ^{210}Pb was only 8% of that of ^{210}Po . During the latter period, the total activity input (and hence the emission of ^{210}Po) was significantly lower, but the emission of ^{210}Pb rose to 41% of that of ^{210}Po .

Measurements have shown that the AMADs of the dust particles to which the radionuclides are attached are typically 0.5–1 μm and that the most appropriate lung absorption class is S. The committed effective dose per unit inhaled intake was determined from leaching tests to be 4.3 $\mu\text{Sv/Bq}$ for ^{210}Pb and 3.6 $\mu\text{Sv/Bq}$ for ^{210}Po [296]. A dose assessment conducted in 1998 showed that the inhalation dose received by a member of the public located in a village 4 km distant was 0.020 mSv/a [289]. Without the recycling of precipitator dust to the sintering plant, it was calculated that this dose would have been 2–5 times lower.

13.4.1.2. Ingestion exposure

Doses received by members of the public living near the TIBV plant were assessed by examining the following exposure pathways [289]:

- (a) Ingestion of radioactive fallout from discharges into the atmosphere:
 - (i) Soil→crops→humans;
 - (ii) Soil→grass→cattle→milk→humans;
 - (iii) Soil→grass→cattle→meat→humans;
 - (iv) Water→shellfish/crustaceans→humans;
 - (v) Water→fish→humans.
- (b) Ingestion of radioactivity discharged into the surface water environment:
 - (i) Water→shellfish/crustaceans→humans;
 - (ii) Water→fish→humans.

TABLE 42. EMISSIONS of ^{210}Pb AND ^{210}Po FROM THE TIBV THERMAL PHOSPHORUS PLANT [292–295]

Period	Ore input (million t)	Proportion of Florida ore (%)	^{210}Po activity (GBq)		^{210}Pb activity (GBq)	
			Input	Emission	Input	Emission
1994–1995	1.186	58	1250.7	1008.9	1250.7	80.1
2002–2003	1.147	0.0	723.5	775.5	723.5	315.0

TABLE 43. RADIONUCLIDE CONCENTRATION FACTORS
USED FOR ASSESSING INGESTION DOSES

Radionuclide	Concentration factor		
	Mussels	Shrimps	Fish
^{210}Po	1000	50 000	2000
^{210}Pb	1000	1000	200

The concentration factors used for determining the activity concentration of radionuclides in marine organisms are given in Table 43. Radionuclide decay and ingrowth were taken into account in the dose assessment. The ingestion dose coefficients for ^{210}Pb and ^{210}Po were 0.69 and 1.2 $\mu\text{Sv/Bq}$, respectively, as specified in the BSS [2]. The results of the assessment showed that the dose arising from ingestion of radionuclides discharged from the TIBV plant was very small — about 0.001 mSv/a.

13.4.2. Use of calcium silicate slag

13.4.2.1. Road construction

The use of calcium silicate slag as a construction material is subject to the requirements for existing exposure situations (see Section 3.1.1 and Ref. [2]). In terms of these requirements, workers are regarded as members of the public for the purposes of radiation protection. The exposure of workers involved in the construction of roads using calcium silicate slag is reported in Ref. [296]. Construction workers are exposed to gamma radiation from the material. The radionuclides ^{214}Pb and ^{214}Bi together contribute 99% of the total gamma dose. The external gamma dose rate 1 m above the mid-point of a layer of phosphorus slag 20 m square and 0.4 m thick was estimated, assuming the ^{238}U and ^{232}Th series radionuclides in the phosphorus slag to be in equilibrium with their respective parents. For ^{238}U series radionuclides, the dose rate was found to be 0.28 $\mu\text{Sv/h}$ per unit activity concentration (in becquerels per gram). The corresponding dose rates for ^{232}Th series radionuclides and ^{40}K were 0.43 and 0.03 $\mu\text{Sv/h}$, respectively. These could be taken as maximum values, as increasing the dimensions of the slag layer had no effect on the dose rates. In practice, the average dose rate applicable to road construction workers is significantly lower, for the following reasons:

- (a) The shielding effect of machines used in road construction reduces the dose rate to the operator by 50%.

- (b) The width of most roads is less than 20 m.
- (c) The worker is not always in the centre of the road bed; the dose rate at the edge is approximately 50% lower.

On the basis of these practical considerations and measurements taken at a road construction site in the Netherlands, and assuming an annual exposure time of 1600 h, the effective dose received in a year by a road construction worker from gamma radiation originating from the slag was estimated to be 0.25 mSv per unit activity concentration of ^{238}U in the slag. The corresponding doses for ^{232}Th and ^{40}K were, respectively, 0.388 and 0.025 mSv per unit activity concentration. Assuming realistic dust levels, sustained for the same annual exposure period of 1600 h, the annual committed effective dose from the inhalation of airborne slag particles was estimated to be 0.03 mSv per unit activity concentration of ^{238}U or ^{232}Th (the same value applied to each radionuclide). The inhalation dose from ^{40}K was negligible. Assuming an ^{238}U activity concentration of 2 Bq/g (which is at the upper end of the normal range in phosphorus slag) and ^{232}Th and ^{40}K activity concentrations each of 0.05 Bq/g, the annual effective dose was thus 0.52 mSv from external gamma exposure and 0.06 mSv from dust inhalation, giving a total annual effective dose of 0.58 mSv.

During road construction, a nearby resident may be exposed to dust, but only for a few hours per day and for a construction period in that person's neighbourhood of a few days to a few weeks in the year of construction. Consequently, comparing the situation with that for a road construction worker, the maximum dose received by a member of the public as a result of the inhalation of phosphorus slag particles during road construction will be no more than a few microsieverts only in that year or those years in which construction work is carried out in that person's neighbourhood.

Once the road is constructed, a member of the public may be exposed to external gamma radiation through the use of that road. Doses received as a result of the incorporation of phosphorus slag from the TIBV plant into roads in the Netherlands have been estimated [296]. It was assumed that the exposure occurs in the middle of the road and that the phosphorus slag layer has a thickness of 0.4 m and a ^{238}U activity concentration of 1.25 Bq/g. The top layer of the road surface, which never contains phosphorus slag, was assumed to have a density of 2350 kg/m³ and a thickness ranging from 0.06 to 0.19 m, depending on the type of road. The maximum exposure time is limited by the fact that the slag production level of the TIBV plant (600 000 t/a) accounts for less than 4% of the total road bed construction material required in the Netherlands. Therefore, the average exposure time was assumed to be 1.5 h per day. On the basis of these assumptions, the annual dose received by a member of the public was estimated to be about 0.060 mSv for a top layer thickness of 0.06 m, about 0.020 mSv for a

top layer thickness of 0.13 m, and about 0.001 mSv for a top layer thickness of 0.19 m. These dose estimates are likely to be valid for both private and commercial road users. Commercial road users may spend more time on the road, but such time is usually spent on major highways, which have more than one top layer to obtain the necessary construction strength.

13.4.2.2. Dyke construction

A study commissioned by the Dutch Ministry of the Environment investigated the leaching behaviour of the radionuclides in phosphorus slag with a view to determining the radiological impact of using such material in the construction of dykes [289]. In a hypothetical situation in which all the dykes of the IJsselmeer (the largest lake in the Netherlands) were assumed to have been constructed using phosphorus slag as a filler material, the maximum annual dose received by a member of the public was calculated to be 0.000 012 mSv; an insignificant level.

13.4.2.3. House construction

In principle, phosphorus slag can be considered for use in house construction and in this regard should be treated no differently from other potential construction materials containing elevated levels of natural radionuclides. However, any such application requires careful assessment on a case-by-case basis. The annual dose received by a house occupant depends on the activity concentration of the material and the nature and extent of its incorporation into the structure of the house. Two contrasting situations are highlighted in Ref. [289]. The use of phosphorus slag in very large quantities could be an unacceptable option because of doses being considerably higher than those associated with normal construction materials. As an extreme example, residing for a year on a surface formed entirely by a thick layer of phosphorus slag is estimated to give rise to an annual dose of 5 mSv. On the other hand, the incorporation of phosphorus slag into concrete used for foundation piles could be an acceptable option.

13.5. REGULATORY CONSIDERATIONS

The radionuclide activity concentrations in the phosphate rock feedstock and the calcium silicate slag may, in some cases, exceed 1 Bq/g by a moderate amount. In facilities that recycle the furnace dust extracted from the precipitator, the activity concentrations of ^{210}Pb and ^{210}Po may increase to several hundred

becquerels per gram as they progressively accumulate in this dust. Consequently, in terms of the Standards, the production of phosphorus by the thermal process should be considered for regulatory control as a practice. The annual doses received by plant workers are less than 1 mSv, although there is clearly potential for doses several times higher if airborne dust in the furnace area is not adequately controlled. The decay storage of precipitator dust prior to its eventual disposal needs to be carried out under controlled conditions because of the high activity concentrations involved. The annual doses received by members of the public from discharges from the plant have been determined to be far below 1 mSv. The most appropriate regulatory option is likely to be a requirement for authorization, most probably in the form of a registration.

When using the calcium silicate by-product for the construction of structures such as roads and dykes, the doses received annually by construction workers and members of the public are far below 1 mSv and no restrictions on such use would appear to be necessary. The use of the material in the construction of dwellings, while not having been studied specifically, would appear to have the potential for giving rise to doses exceeding 1 mSv because of the likelihood of shorter exposure distances and longer exposure periods. Therefore, a situation specific dose assessment would be needed to determine the need for any restrictions on such use.

Appendix I

URANIUM AND THORIUM DECAY SERIES

The ^{238}U and ^{232}Th series are the main decay series of interest. The ^{235}U decay series is less important for radiation protection purposes, except for the radionuclide ^{227}Ac , which can contribute significantly to inhalation exposure. If necessary, the presence of ^{235}U (and, by implication, its decay progeny) can be taken into account on the basis of the abundances of ^{235}U and ^{238}U in natural uranium (0.711 and 99.284%, respectively) — the corresponding ^{235}U : ^{238}U activity ratio is 0.046. Details of the ^{238}U and ^{232}Th decay series, as reported in Ref. [297], are given in Tables 44 and 45, respectively.

TABLE 44. URANIUM-238 DECAY SERIES

	Half-life	Mode of decay ^a	Gamma energy (keV) ^b
^{238}U	4.468×10^9 a	Alpha	
^{234}Th	24.10 d	Beta	63.29 (4.8%), 92.38–92.8 (5.6%)
$^{234\text{m}}\text{Pa}$	1.17 min	Beta	1001.03 (0.837%)
^{234}U	245 700 a	Alpha	
^{230}Th	75 380 a	Alpha	
^{226}Ra	1600 a	Alpha	186.211 (3.59%)
^{222}Rn	3.8235 d	Alpha	
^{218}Po	3.10 min	Alpha	
^{214}Pb	26.8 min	Beta	351.932 (37.6%)
^{214}Bi	19.9 min	Beta	609.312 (46.1%), 1764.491 (15.30%)
^{214}Po	164.3 μs	Alpha	
^{210}Pb	22.20 a	Beta	46.539 (4.25%)
^{210}Bi	5.012 d	Beta	
^{210}Po	138.376 d	Alpha	
^{206}Pb	Stable	—	

^a Only major modes of decay are shown.

^b Only major gamma emissions of interest are shown.

TABLE 45. THORIUM-232 DECAY SERIES

	Half-life	Mode of decay ^a	Gamma energy (keV) ^b
²³² Th	1.405 × 10 ¹⁰ a	Alpha	
²²⁸ Ra	5.75 a	Beta	
²²⁸ Ac	6.15 h	Beta	911.204 (25.8%), 968.971 (15.8%)
²²⁸ Th	1.912 a	Alpha	
²²⁴ Ra	3.66 d	Alpha	240.986 (4.10%)
²²⁰ Rn	55.6 s	Alpha	
²¹⁶ Po	0.145 s	Alpha	
²¹² Pb	10.64 h	Beta	238.632 (43.6%)
²¹² Bi	60.55 min	Beta 64.06% Alpha 35.94%	727.330 (6.67%)
²¹² Po	0.299 μs	Alpha	
²⁰⁸ Tl	3.053 min	Beta	583.191 (84.5%), 2614.533 (99.16%)
²⁰⁸ Pb	Stable	—	

^a Only major modes of decay are shown.

^b Only major gamma emissions of interest are shown.

Appendix II

COMPOSITION OF PHOSPHATE ORES

Data on the composition of phosphate ores are given in Table 46 for the main chemical constituents, Table 47 for heavy metals and Table 48 for radionuclides. Some values have been rounded. The values reported are not necessarily representative of ores currently exploited. The ores are of sedimentary origin except where stated otherwise.

TABLE 46. MAIN CHEMICAL CONSTITUENTS OF PHOSPHATE ORES (BY COUNTRY)

(from Refs [298, 299] except where stated otherwise)

Country	Concentration (%)							
	P ₂ O ₅	CaO	SiO ₂	MgO	Al ₂ O ₃	Fe ₂ O ₃	F	CO ₂
Algeria	24–28							
Australia [300]	23							
Brazil ^a	8–34	24–45	11–30	0.1	2.8–8.4	2.4–3.5	1.6–2.6	
China:								
Guangxi ^b	8–16	14–24	40–54	0.3–0.5	7.4–11	3.1–5	0.9–1.3	0.4–1.7
Guizhou	22–36	52–53	3–4	2.5–3.5		1.5–1.8	3–4	
Hubei ^c	15–35	23	42	4.0	7.7	2.5	0.9	8.2
Hunan	<20–26							
Sichuan	17–28	7–39	4.1–5.7	0.15–0.7	4.7–28	2.1–8.4	0.3–2.5	0.8–1.8
Yunnan	24–32			0.6–0.7				
Egypt:								
Nile Valley	18–30	34–46	12–29	0.2–0.4	0.5–1.9	2.7–3.3	2.6	4.6–26
Red Sea	9.2–33	7.3–45	2–4.2	0.5–5.2		1.3–1.6	2.8–3.1	5.7–18
Abu Tartur ^d	29							
India [30]:								
Mussorie	15							
Cuddapah	0.5–28							
Karnataka	10–30							

TABLE 46. MAIN CHEMICAL CONSTITUENTS OF PHOSPHATE ORES
(BY COUNTRY) (cont.)

(from Refs [298, 299] except where stated otherwise)

Country	Concentration (%)							
	P ₂ O ₅	CaO	SiO ₂	MgO	Al ₂ O ₃	Fe ₂ O ₃	F	CO ₂
Israel	20–30							
Jordan	13–36	48 [301]	17–32 [301]					
Morocco	25–33; 22–28 [302]							
Russian Federation (Kola) (igneous)	4–31						1–3 [303]	
Senegal	15–39 [304]	8–47	12–45	0.8–5.2	0.5–32	0.5–10		
South Africa (igneous)	6–10 [304]							
Syrian Arab Republic	18–28							
Togo	26–30	41	9.4		10	2.1		
Tunisia	11–35							
Uganda (igneous)	30–40; 8–35 [304]	54	1.4		1.7	0.5	3.1; 1.5–4.4 [304]	
United Republic of Tanzania ^e	<20–30	44	4.2	2.1	1.4	0.9	2.9; ≤4 [304]	4.9
USA:								
Florida and North Carolina [305, 306]	9–14							
Idaho and Utah [305, 306]	22–24							
South Carolina	22							

^a Na₂O: 0.2%; K₂O: 1%.

^b Na₂O: 0.01–0.05%.

^c K₂O: 3.8%.

^d Rare earth elements: 0.2%.

^e Na₂O: 0.5%.

TABLE 47. HEAVY METALS IN PHOSPHATE ORES (BY COUNTRY)
(from Refs [298, 299] except where stated otherwise)

Country	Concentration (ppm)							
	Sr	Mn	Zn	Cd	V	Cr	Ba	Ti
Brazil		2600						
China:								
Guangxi					36–880			
Guizhou				10–30				
Hubei		14 000						
Sichuan	15 000–48 000				60–90			
Egypt (Nile Valley)			177	5	94	86		
South Africa (igneous) [307]								23 000–35 000
United Republic of Tanzania [304]	2500–9900						1100–2100	
USA (Idaho)					110–530	67–670		

TABLE 48. RADIONUCLIDES IN PHOSPHATE ORES (BY COUNTRY)

Country	Activity concentration (Bq/g)						
	²³⁸ U	²³⁰ Th	²²⁶ Ra	²³² Th	²²⁸ Ra	²²⁸ Th	⁴⁰ K
China (Guangxhi) [298]	0.6–1.1						
Egypt (Nile Valley) [298]	0.7						
Morocco [304]	1						
Pakistan (Hazara) [51]			0.4			0.05	0.27
Russian Federation (Kola) (igneous) [15, 308]	0.07			0.1			0.1
South Africa (igneous) ^a	0.2		0.2	0.4		0.4	
Sudan [309]:							
Uru			4 (1.2–15)	0.01 (0.001–0.02)			0.06 (0.01–0.1)
Kurun			0.4 (0.15–0.8)	0.01 (0.002–0.02)			0.1 (0.06–0.36)
Syrian Arab Republic [52]	0.75–1.5						
United Republic of Tanzania [49, 310]	0.02–11	0.03–4.5	5.8	0.007–1.1	0.5	0.15–1.1	
USA:							
Central Florida [16, 46, 47, 311, 312]	0.75–3.1	1.3	0.7–3.1	0.02			0.003–0.019
Northern Florida [47]	0.06–0.1		0.2–0.5				
North Carolina [304]	0.6						

^a Derived from values reported for phosphate rock (Appendix IV) and tailings (Table 8).

Appendix III

PHOSPHATE-CONTAINING PRODUCTS AND THEIR APPLICATIONS

TABLE 49. FOOD AND PHARMACEUTICAL APPLICATIONS

Product and chemical formula	Application
<i>Phosphoric acid</i>	
Orthophosphoric acid, H_3PO_4 in H_2O	Acidulent in cola beverages; sugar refining; acid flavouring agent in jams and jellies; ingredient in bread dough and cake flour; yeast nutrient; cottage cheese production
<i>Ammonium phosphates</i>	
MAP, $\text{NH}_4\text{H}_2\text{PO}_4$	Buffer capacity; nutrient source; brewing
DAP, $(\text{NH}_4)_2\text{HPO}_4$	Buffer; nutrient source; dough strengthener; firming agent; processing aid; biscuits; brewing; sugar refining; ingredient in dentifrice
<i>Calcium phosphates</i>	
MCP, $\text{Ca}(\text{H}_2\text{PO}_4)_2$ or $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	Anhydrous: Bakery applications, including self-raising flour, phosphated flour, self-raising corn meal, consumer prepared mixes and baking powder; calcium supplement in foods Monohydrate: Acidulent for foods and beverages; leavening acid; nutrient; dietary supplement; yeast food dough conditioner
DCP, CaHPO_4 or $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	Excipient for tableting; polishing ingredient in dentifrice; mineral, dietary and nutritional supplements Dihydrate: Nutrient; yeast food; leavening agent
Tricalcium phosphate, $\text{Ca}_3(\text{OH})(\text{PO}_4)_3$	Flow promoter for powders; suspension polymerization agent; nutritional mineral supplement; ingredient in dentifrice
<i>Magnesium phosphates</i>	
Magnesium phosphate, MgHPO_4 , $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$	Heat activated leavening agent; ingredient in baked goods including cakes, muffins, biscuits and pancakes
Dimagnesium phosphate, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$	Nutrient source; pH control agent; dietary supplement; flow aid

TABLE 49. FOOD AND PHARMACEUTICAL APPLICATIONS (cont.)

Product and chemical formula	Application
<i>Sodium phosphates</i>	
Monosodium phosphate, NaH_2PO_4	Buffer and emulsifier in food preparation; acid ingredient in effervescent powders and laxatives; acidifier in non-cola beverages; buffers the pH of cheese and interacts with milk proteins to promote emulsification; gelling aid in desserts; prevents discoloration of mixtures of egg whites and yolks
Disodium phosphate, Na_2HPO_4 or $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$	Anhydrous: Buffer; emulsifier or texturizer for instant puddings, evaporated milk, processed cheese, cereals, pre-cooked meats and pasta products; pharmaceuticals; water treatment in food processing Dihydrate: Emulsifier, especially for processed cheese; texturizer; buffer; nutritional mineral supplement
Trisodium phosphate, Na_3PO_4 or $4(\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}) \cdot \text{NaOH}$	Processed cheese and cheese products; quick cooking cereals; meat, poultry and cheese processing; post-chill antimicrobial treatment for raw poultry; clarifier in sugar mills
Sodium acid pyrophosphate, $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$	Leavening acid for baking powder; cake mixes; refrigerated or frozen dough and cake doughnuts; additive to non-dairy creamers; protects processed potatoes from iron induced darkening; decreases or prevents the formation of struvite crystals in albacore tuna; accelerates the development of a red colour in emulsion type meat products; emulsifying agent in cheese processing
Tetrasodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$	Production of metal pyrophosphates; dispersant in malted milk powders; coagulant in instant puddings; colour and moisture retention in processed meats; prevents the formation of struvite crystals in canned seafoods and ice crystals in ice cream
Glassy sodium polyphosphates, sodium hexametaphosphates, $\text{Na}_{(n+2)}\text{P}_n\text{O}_{(3n+1)}$	Sequestration of multivalent ions to inhibit oxidative rancidity in food; water binding in cured meats and reduction of moisture loss during thawing and cooking of poultry and pork; emulsifies fat and protein; water treatment agent to prevent staining of the exterior of canned meat and poultry; scalding agent for meat and poultry; suspension agent in food
Sodium trimetaphosphate, $(\text{NaPO}_3)_3$	Food processing; starch modification; esterification of food starch; pharmaceuticals
Sodium aluminium phosphate, $\text{Na}_3\text{Al}_2\text{H}_{15}(\text{PO}_4)_8$	Heat triggered leavening acid used in bakery products such as refrigerated and frozen products; commercial baking powders and prepared mixes

TABLE 49. FOOD AND PHARMACEUTICAL APPLICATIONS (cont.)

Product and chemical formula	Application
<i>Potassium phosphates</i>	
Dipotassium phosphate, K_2HPO_4	Nutrient for antibiotic production; pharmaceutical aid (buffering agent); emulsifier in non-dairy coffee creamers; cheese processing
Tripotassium phosphate, K_3PO_4	Emulsifier; alkaline buffer; pharmaceuticals
Potassium tripolyphosphate, $K_5P_3O_{10}$	Meat treatment for moisture binding; emulsifier and suspension agent in food
<i>Phosphate blends</i>	
Sodium acid pyrophosphate + calcium chloride, $Na_2H_2P_2O_7$, $CaCl_2$; l-ascorbic acid, $C_5H_8P_2O_7$; Citric acid, $C_3H_4(OH)(COOH)_3 \cdot H_2O$	Maintains the colour, texture and quality of fresh fruit and vegetables; increases the useful shelf life of most treated foods; delays the onset of oxidative and enzymatic browning
Disodium or trisodium phosphate + sodium metaphosphate, Na_2HPO_4 or Na_3PO_4 , $(NaPO_3)_n$, $n = 1000-5000$	Emulsifying agent in pasteurized processed cheese; protein modifier; improves viscosity, melt spread, body and hardness
Sodium aluminium phosphate + MCP, $Na_3Al_2H_{15}(PO_4)_8$, $Ca(H_2PO_4)_2$ or $Ca(H_2PO_4)_2 \cdot H_2O$, $CaCO_3$, SiO_2	Anhydrous: Double acting leavening agent in self-raising flour, self-raising corn meal and biscuit mixes for a full volumed, light product Monohydrate: Acidulent and leavening agent in bakery applications such as pancakes, waffles, cakes and other prepared mixes; adding to the structure resiliency, crumb whiteness and baking tolerance of white cake mixes
Polyphosphate blends, $Na_5P_3O_{10}$ $Na_{(n+2)}P_nO_{(3n+1)}$, $n = 10-16$	Sequestration of multivalent metal ions to inhibit oxidative rancidity; reduces moisture loss during thawing and cooking; emulsifies fat and protein; improves solubility; improves gelation properties in surimi; gives a neutral pH and improves emulsion stability
<i>Phosphorus chlorides and oxides</i>	
Phosphorus trichloride, PCl_3	Intermediate in the manufacture of phosphate esters used in the production of several pharmaceuticals
Phosphorus pentachloride, PCl_5 and phosphorus oxychloride, $POCl_3$	Chlorinating agent used in the production of antibiotics
Phosphorus pentoxide, P_2O_5	Used in various organic synthesis reactions to produce intermediates for pharmaceuticals

TABLE 50. INDUSTRIAL, AGRICULTURAL AND DOMESTIC APPLICATIONS

Product and chemical formula	Application
<i>Phosphoric acid</i>	
Orthophosphoric acid, H_3PO_4 in H_2O	Commercial grade: Manufacture of phosphates and fertilizers; acid cleaners; aluminium brighteners; metal phosphatizing; cement processing; leather tanning; fire bricks, silica bricks, crucibles and moulds; dental cements; opal glass and special glasses, such as that for sodium lamps; toilet preparations; varnish; synthetic rubber; boiler water treatment; potable water treatment Furnace grade: Semiconductor etchant; printed circuit board cleaner; reagent for analytical chemistry
Polyphosphoric acid, $\text{H}_{n+2}\text{P}_n\text{O}_{3n+1}$ Superphosphoric acid (mixture of ortho- and polyphosphoric acids)	Production of phosphates, phosphate esters; phosphorylation of polyols; metal cleaning and phosphatizing; aluminium brightening; electrolyte for fuel cells; refractory bonding; catalyst in organic reactions such as rearrangements, polymerization, dehydration, hydrolysis, nitration, bromination and cyclization
<i>Ammonium phosphates</i>	
MAP, $\text{NH}_4\text{H}_2\text{PO}_4$	Liquid and dry speciality fertilizer; fire and afterglow retardant; bonding agent in ceramics; corrosion inhibitors
DAP, $(\text{NH}_4)_2\text{HPO}_4$	Liquid and dry speciality fertilizer; fire and afterglow retardant; bonding agent in ceramics; corrosion inhibitors; welding of tin, copper, brass and zinc
<i>Calcium phosphates</i>	
MCP, $\text{Ca}(\text{H}_2\text{PO}_4)_2$ or $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	Feed; fertilizer; opaque glass manufacture; paint preparations for steel enamels
DCP, CaHPO_4 or $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	Feed; mineral supplement; inner coating of fluorescent lamps; glass manufacture
Tricalcium phosphate, $\text{Ca}_3(\text{PO}_4)_3$	Feed; flow conditioning and anticaking agent; flow agent in dry powder fire extinguishers; additive to glues and resins in manufacture of plywood and granulated fertilizers; expandable polystyrene manufacture; fluorescent lamps; whitening of porcelain; enamels; glass manufacture

TABLE 50. INDUSTRIAL, AGRICULTURAL AND DOMESTIC APPLICATIONS (cont.)

Product and chemical formula	Application
<i>Sodium phosphates</i>	
Monosodium phosphate, NaH_2PO_4	Metal cleaning and phosphatizing compounds; boiler water conditioning; dyeing of cotton; mineral supplement; buffer in electroplating; dairy cleaner to remove milkstones; feed supplement; shampoos
Disodium phosphate, Na_2HPO_4 or $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$	Pigments; enamels; ceramics; detergents; welding Anhydrous: Boiler water conditioning; potable water treatment; phosphatizing metal cleaner; buffering agent in textile dye baths
Trisodium phosphate, Na_3PO_4 or $4(\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}) \cdot \text{NaOH}$	Anhydrous: Industrial and household cleaners; potable water treatment; bottle washing; textile washing; dyeing and bleaching; photographic film developer bath ingredient; builder and filler for soaps; paint remover; metal degreasing Dodecahydrate: Ingredient in alkaline cleaners to emulsify fats, greases and oils; buffering at high pH
Sodium acid pyrophosphate, $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$	Acid cleaners; metal polishes; oil well drilling muds; buffer; detergents; iron phosphatizing; dairy cleaner to remove milkstones; pigment dispersant in water based paints
Tetrasodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$	Detergents and soaps; dispersant in clay processing; oil well drilling mud conditioner; water conditioning and textile processing; pitch control in paper mills; bleach bath stabilizer; alkaline metal cleaners; paper coating and filling; soil stabilization; manufacture of plastic granules for injection moulding
Glassy sodium polyphosphates, sodium hexametaphosphates, $\text{Na}_{(n+2)}\text{P}_n\text{O}_{(3n+1)}$	Industrial water treatment; potable water treatment; dispersion of pigmenting and dyeing operations in the textile industry; film development; oil well drilling mud deflocculant; sequestrant and suspension agent in clay processing; detergents; refractory binding
Sodium tripolyphosphate, $\text{Na}_5\text{P}_3\text{O}_{10}$ or $\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$	Anhydrous: Consumer and industrial cleaning products; detergents, such as for dishwashers, laundry and vehicle washing; potable water treatment; personal care products such as bath beads; clay slurry deflocculation; soil stabilization; cement manufacture; flotation reagent in mining; pitch control in wood pulping; textile operations Hexahydrate: Ingredient in compounds where rapid solubility or freedom from caking is essential; bath water conditioners
Sodium trimetaphosphate, $(\text{NaPO}_3)_3$	Consumer and industrial detergents and cleaning products; control of product density; dry bleach bases; phosphate detergent intermediate; potable water treatment

TABLE 50. INDUSTRIAL, AGRICULTURAL AND DOMESTIC APPLICATIONS (cont.)

Product and chemical formula	Application
<i>Potassium phosphates</i>	
Monopotassium phosphate, KH_2PO_4	Seedbed fertilizer supplements; speciality and household fertilizers; nutrient for bacteria in biological waste treatment; potable water treatment; buffer capacity
Dipotassium phosphate, K_2HPO_4	Corrosion inhibitor in antifreeze; enamel production and paper processing; liquid fertilizers; potable water treatment; dispersion medium in liquid detergents
Tripotassium phosphate, K_3PO_4	Rubber processing; industrial and household cleaners; water conditioning; bottle washing; textile washing; dyeing and bleaching; photographic film developer bath ingredient; builder and filler for soaps; paint remover; metal degreasing
Potassium tripolyphosphate, $\text{K}_5\text{P}_3\text{O}_{10}$	Pigment dispersion in latex emulsion paints; sequestrant in liquid detergents; suspension agent; speciality boiler water compounds
Tetrapotassium pyrophosphate, $\text{K}_4\text{P}_2\text{O}_7$	Builder for liquid detergents and liquid potash soaps; synthetic rubber; buffer and sequestrant in electroplating baths; speciality boiler compounds; dispersant in water based paints; emulsifier of oils and greases; deflocculant in oil well drilling muds
<i>Phosphate blends</i>	
Sodium potassium polyphosphates	Builder for liquid consumer and industrial cleaning products
<i>Phosphorus sulphides</i>	
Phosphorus sesquisulphide, P_4S_3	Safety matches
Phosphorus pentasulphide, P_4S_{10}	Petroleum and lubricant additive intermediate; insecticide intermediate; ore flotation reagent; reaction with alcohols, mercaptans, amines and organic acids to produce thiophosphorus derivatives

TABLE 50. INDUSTRIAL, AGRICULTURAL AND DOMESTIC APPLICATIONS (cont.)

Product and chemical formula	Application
<i>Phosphorus chlorides and oxides</i>	
Phosphorus trichloride, PCl_3	Intermediate in the manufacture of phosphate esters (used in plasticizers, hydraulic fluids, flame retardants and as a cryoscopy solvent), organophosphorus pesticides, organophosphines, phosphorus oxychloride, surfactants, stabilizers, defoamers and paper products; chlorinating agent; production of special metallic deposits
Phosphorus pentachloride, PCl_5	Chlorinating agent in the manufacture of dyes; catalyst for the condensation and cyclization reaction and to improve the grain structure of light-metal castings; production of materials by the agricultural industry; key ingredient in specialized fire retardants
Phosphorus oxychloride, POCl_3	Production of cosmetics and flame retardants
Phosphorus pentoxide, P_2O_5	Use in various organic synthesis reactions to produce intermediates for speciality chemicals; production of phosphate esters; drying agent (making use of its hygroscopic properties)

Appendix IV

COMPOSITION OF PHOSPHATE ROCK

Data on the composition of phosphate rock are given in Table 51 for the main chemical constituents, Table 52 for heavy metals and Table 53 for radionuclides. Some values have been rounded. The values reported are not necessarily representative of current production. The phosphate rock is derived from ore of sedimentary origin except where stated otherwise.

TABLE 51. MAIN CHEMICAL CONSTITUENTS OF PHOSPHATE ROCK (BY COUNTRY)

Country	Concentration (%)										Reference
	P ₂ O ₅	CaO	SiO ₂	MgO	Al ₂ O ₃	Fe ₂ O ₃	F	CO ₂	Na ₂ O	K ₂ O	
Algeria	29–31										[298, 305]
Australia	23										[305]
Brazil	35–36										[298]
China:											
Guizhou	28–36	45–52	3–10	0.7–2	1.3–1.8	1.3–1.8	4	5	0.5–1	0.5	[313]
Hubei	30–34	44–48	8	0.6–1.2	1.5a	1.5 ^a					[314]
Sichuan	33	47	—	0.6	1.2	1.2	3		0.35	0.4	[315]
Egypt	29										[305]
India	30										[305]
Iraq	30										[305]
Israel	32–33										[298, 305]
Jordan	30–34										[301]
Morocco ^b	33–35	43–51	1.9–8.2	0.3–0.6	0.4–1.7	0.2–0.3	4	4.5	0.5–0.7	0.1–0.2	[144, 298, 316]
Russian Federation:											
Briansk	19–30										[305]
Kola (igneous) ^c	35–>40	51	1.1	0.1	0.4	0.3	3.3	0.2	0.4	0.5	[144, 298, 305]
Senegal	32–37	50	5	0.1	1.1	0.9	3.7	1.8	0.3	0.1	[144, 304]

TABLE 51. MAIN CHEMICAL CONSTITUENTS OF PHOSPHATE ROCK (BY COUNTRY) (cont.)

Country	Concentration (%)										Reference
	P ₂ O ₅	CaO	SiO ₂	MgO	Al ₂ O ₃	Fe ₂ O ₃	F	CO ₂	Na ₂ O	K ₂ O	
South Africa (igneous) ^d	36–40	52–54	0.4–2.6	0.4–1.5	0.06–0.1	0.2–0.5	2.2–2.6	0.9–4.3	0.2	0.01–0.06	[48, 144, 304]
Syrian Arab Republic	30										[52, 305]
Togo	30–37	50–51	4.5–7	0.03–0.1	1	1–1.5	3.8–3.9	1.6	0.2	0.04–0.1	[144, 298, 304, 317]
Tunisia	30										[305]
Uganda (igneous)	40–42										[304]
USA:											
Florida ^e	27–34	50	3.7	0.3–1.25	1.1	1.1	3.9	3.1	0.5	0.1	[144, 318]
Idaho and Utah	27–29										[305, 306]

^a Al₂O₃ and Fe₂O₃ concentrations assumed to be equal.

^b Rare earth elements: 0.09%.

^c Rare earth elements: 0.6%.

^d Rare earth elements: 0.5%.

^e Rare earth elements: 0.06%.

TABLE 52. HEAVY METALS IN PHOSPHATE ROCK (BY COUNTRY)

Country	Concentration (ppm)										Reference
	Sr	Mn	Co	Ni	Zn	Cd	Hg	Cu	Pb	As	
Algeria	1800–2800	17–30	11	28	88–150	10–19	0.004	10–16	1.1–2.7	8	[319, 320]
China:											
Guizhou						3	5–6				[313]
Sichuan						0				80	[315]
Egypt (Abu Tartur)		1225	17	20	190	2.6–21		10	33	17	[319, 320]
Israel	120–2700	7–440	10	61–80	29–630	1.5–36	0.002	8–31	2.3–5.8		[319, 320]
Jordan	1100–2200	9–285	8.5–12	20–71	85–420	2.7–35		9–27	1–2.3	2.6–28	[319]
Morocco ^a	625–1000			35–44	155–400	<2–55	0.1	4–40	1–10	13	[144, 316, 320]
Russian Federation:											
Briansk					30	1			1.5	3.4	[319]
Kola (igneous) ^b	29 000–30 000	26	4	2–15	20–25	0.1–1.2	0.004–33	15–37	1.8	2–10	[144, 319, 320]
Senegal ^c						<5–115	0.2		5	18	[144, 304]
South Africa (igneous)	4500–4600	138–160	10	2–20	6–11	0.04–2	0.1–<0.2	90–200	11–18	8.7–13	[48, 144, 319, 320]
Syrian Arab Republic	1900	6–6.5	8	54–61	320–340	3.9–16		5–29	2–3.5	2.1–11	[319, 320]
Togo	1000	230				48–67	0.6			12	[144, 304, 315, 317]
Tunisia	4100	33	4.7	15	22–120	21–52		11	1.7–2	5.7	[319, 320]
Uganda (igneous)	4900	1350	90	100	290	0.25		33	9		[319]

TABLE 52. HEAVY METALS IN PHOSPHATE ROCK (BY COUNTRY) (cont.)

Country	Concentration (ppm)								Reference		
	Sr	Mn	Co	Ni	Zn	Cd	Hg	Cu		Pb	As
USA:											
Florida ^e				28	70	6–10	0.02	13	17	11	[144, 320]
North Carolina						37–51					[320]

^a Cr: 200 ppm; V: 160 ppm; Y: 50 ppm.
^b Cr: 19 ppm.
^c Cr: 6 ppm.
^d Bi: <2 ppm; Cr: 1 ppm; V: 16 ppm.
^e Cr: 60 ppm.

TABLE 53. RADIONUCLIDES IN PHOSPHATE ROCK (BY COUNTRY)

Country	Activity concentration (Bq/g)							Reference
	²³⁸ U	²³⁰ Th	²²⁶ Ra	²¹⁰ Pb	²¹⁰ Po	²³² Th	²²⁸ Ra	²²⁸ Th
Algeria	0.65–0.9		0.5–0.6			0.07–0.09		[48, 91]
Egypt (Nile Valley)	0.5		0.5			0.0004		[321]
Egypt	0.4–0.5		0.3–0.5			0.02–0.04		[311, 322]
India	1.34 (1.0–1.7)		1.32 (1.3–1.4)					[74]
Italy (Gela) ^a			1.24–1.25					[323]
Israel	1.5–2.6		1.5–1.8					[48]
Jordan	0.5–1.9		0.4–0.75	1		0.002–0.02		[48, 51, 91]
Morocco	1.34 (0.9–1.9)	1.5–2.0	0.9–2.0	0.7–1.9	1.7–1.9	0.007–0.03		[48, 74, 86, 98, 144, 308]
Russian Federation (Kola) (igneous) ^b	0.03–0.1		0.02–0.09			0.06–0.09		[48, 292, 293, 308]
Senegal	0.7–1.3		1–1.1	1				[48, 87, 144]
South Africa (igneous)	0.14 (0.11–0.18)		0.14 (0.11–0.16)	0.12 (0.10–0.13)		0.47 (0.33–0.61)	0.55 (0.40–0.62)	[48] (0.45–0.61)
Togo	1–1.5		1.1–1.3	0.9		0.03–0.1	0.05	[48, 98, 308]
Tunisia	0.6		0.5–0.8			0.09–0.29		[48, 91, 308]

TABLE 53. RADIONUCLIDES IN PHOSPHATE ROCK (BY COUNTRY) (cont.)

Country	Activity concentration (Bq/g)						Reference
	²³⁸ U	²³⁰ Th	²²⁶ Ra	²¹⁰ Pb	²¹⁰ Po	²³² Th	
United Republic of Tanzania	4.1–4.6	4.7	5			0.6	[49]
USA:							
Florida	1.5		1.6–2				[292, 293, 324]
Central Florida:							
Pebble	1.3–2.5	2	1.6–3.6			0.03	[16, 47]
Concentrate	0.7–1.8	1.4	1–1.9			0.02	[16, 47]
Overall	1.4–1.5	1.6	1.5–1.6			0.02–0.03	[16, 308]
Northern Florida:							
Pebble	0.3–0.8		0.95–1				[47, 308]
Concentrate	0.1–0.2		0.6–0.8				[47]
Idaho	1.9		1.8			0.03	[308]
South Carolina	4.8–5		4.8–5			0.08	[48, 308]
Utah	1.6		1.9			0.03	[308]
Wyoming	2.3		2.3			0.01	[308]

^a Pa-234m: 1.42–1.46 Bq/g; Pb-214: 1.23–1.26 Bq/g; Bi-214: 1.09–1.17 Bq/g; Pb-212: 0.04 Bq/g.

^b K-40: 0.14 Bq/g.

Appendix V

METHODS OF PHOSPHORIC ACID PRODUCTION USING SULPHURIC ACID DIGESTION

V.1. THE DIHYDRATE (DH) METHOD

The DH method is the most widely used of three so-called ‘weak acid’ methods. The acid digestion is carried out at a temperature of 70–85°C to yield phosphoric acid with a relatively low P_2O_5 content of 24–32% and dihydrate phosphogypsum crystals. A simplified schematic representation of the DH method is shown in Fig. 72.

In order to minimize the amount of unreacted rock remaining within the phosphogypsum, the particle sizes of the feedstock must lie within certain bounds. Some grades of commercial rock already meet this requirement, but most feedstocks require particle size reduction, usually using a ball mill or rod mill. In general, the degree of agitation and the amount of free sulphate in the attack tank determine the amount of milling required — a low free sulphate content and good agitation allows the use of coarser rock particles. Typically, the dihydrate process requires a feedstock particle size distribution in which 60–70% of the particles are less than about 100 μm . Traditional dry milling methods first require the moisture content of the rock to be reduced from 10–15% to, typically, 2%. The energy costs associated with this drying step have encouraged the industry to convert to wet milling, initially using fresh water but more recently making

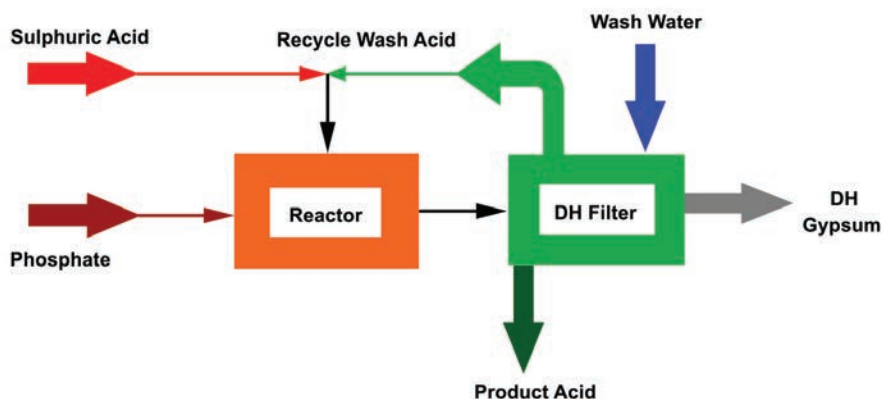


FIG. 72. The DH method [65].

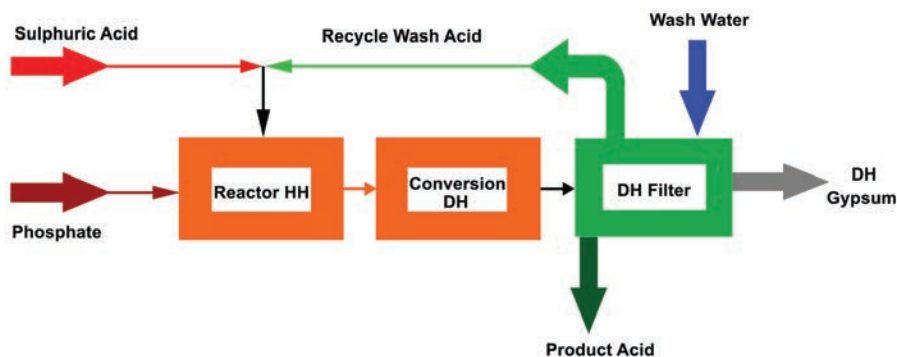


FIG. 73. The HRC method [65].

increased use of the partially neutralized acidic process water ('pond water') recycled from the phosphoric acid production process. In some facilities, the mill liners are manufactured from high alloy materials, allowing the use of 100% pond water without encountering corrosion problems. The use of pond water in this manner reduces the consumption of water and allows the recovery of P_2O_5 .

Although a single attack tank is sometimes used, the reaction system more commonly comprises a series of separate tanks or tank compartments. The phosphogypsum crystals produced from the acid digestion process are separated from the phosphoric acid by vacuum filtration followed by up to four stages of countercurrent washing.

V.2. THE HEMIHYDRATE RECRYSTALLIZATION (HRC) METHOD

The HRC method, the second of the three weak acid methods, resembles that of the multiple reactor dihydrate process, except that the initial attack tank operates under hemihydrate conditions (for instance, at a temperature of 90–110°C). Subsequent attack tanks operate under conditions favouring the rehydration of the hemihydrate phosphogypsum to dihydrate phosphogypsum. The hemihydrate phosphogypsum is recrystallized to the dihydrate form without intermediate hemihydrate separation. The dihydrate crystals are then separated from the phosphoric acid by filtration, as described in Section 5.1.1.1. The method yields phosphoric acid with a P_2O_5 content of 30–32%, no better than that obtainable from the DH method (prior to concentration by evaporation), but the phosphogypsum has a higher level of purity. A simplified schematic representation of the method is shown in Fig. 73.

In a variation of the HRC method, known as the ‘repulping process’, the phosphogypsum is converted back into a slurry and pumped to a second filtration step. The wash water from this second filtration step is returned to the first filtration where it is reused as the wash water for that step. Most of the free acid which is not removed in the first filtration step is removed in the second filtration step. Depending on the amount of free acid, the repulping process can improve the process efficiency by up to 2%. The residual P_2O_5 content of the phosphogypsum is reduced to only 2.5% [85].

V.3. THE DIHYDRATE–HEMIHYDRATE (DH/HH) METHOD

The DH/HH method is the third of the three weak acid methods. The phosphate rock feedstock is digested under dihydrate conditions and the phosphoric acid and dihydrate phosphogypsum are separated by filtration. However, the phosphogypsum crystals, rather than simply being washed at that stage, are instead converted to the hemihydrate form by heating with steam and additional sulphuric acid. The resulting hemihydrate phosphogypsum slurry is filtered and the liquor, containing residual P_2O_5 , is returned to the initial dihydrate process step, thus avoiding the need for achieving a high degree of P_2O_5 recovery during the separation of the acid from the dihydrate phosphogypsum. The hemihydrate recrystallization stage operates at a P_2O_5 concentration of about 20–30% and a sulphuric acid concentration of 10–20%. The phosphoric acid product contains 32–36% P_2O_5 . The P_2O_5 content of the phosphogypsum is only 1% [85]. A simplified schematic representation of the method is shown in Fig. 74.

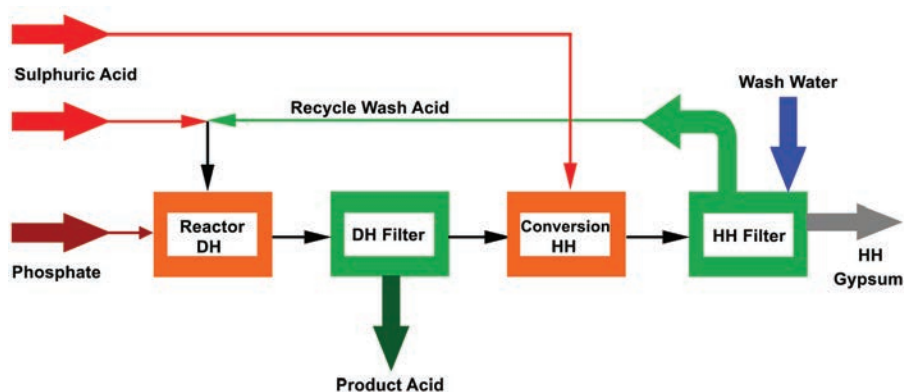


FIG. 74. The DH/HH method [65].

V.4. THE HEMIHYDRATE (HH) PROCESS

The HH process is the first of two so-called ‘strong acid’ methods. The acid digestion conditions are controlled such that the phosphogypsum is precipitated in the hemihydrate form. The reaction temperature, for instance, is 90–110°C, higher than that used for dihydrate phosphogypsum production. Phosphoric acid with a P_2O_5 content of 36–52% is produced directly, resulting in significant energy and cost savings, in that the reaction vessels are similar to those used in the dihydrate method, but the need for prior particle size reduction is minimized or avoided. The P_2O_5 content of the phosphogypsum is relatively high (up to 8% [85]). A simplified schematic representation of the method is shown in Fig. 75.

V.5. THE HEMIDIHYDRATE (HDH) METHOD

The HDH method is the second of the two ‘strong acid’ methods. As with the HH method, the acid digestion conditions are such that the phosphogypsum is precipitated in the hemihydrate form. The hemihydrate crystals are then recrystallized to the dihydrate form and separated by filtration. The filtrate is returned to the process. The phosphoric acid product is removed by filtration at a strength of 42–45%, that is, similar to the values achievable with the HH method but in a narrower range. A simplified schematic representation of the method is shown in Fig. 76.

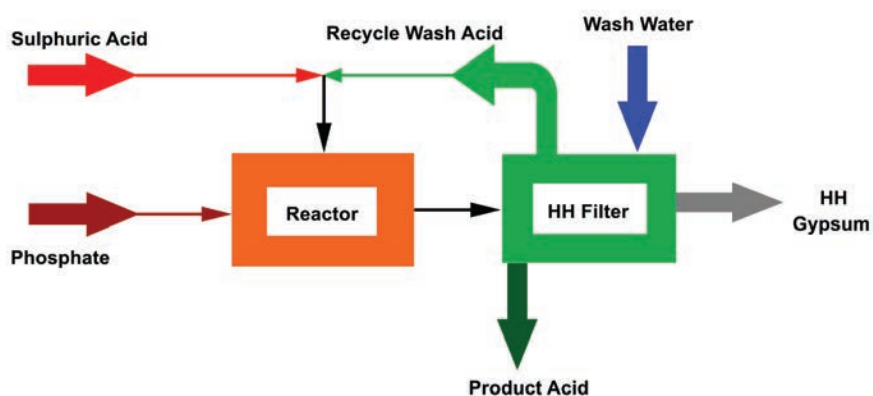


FIG. 75. The HH method [65].

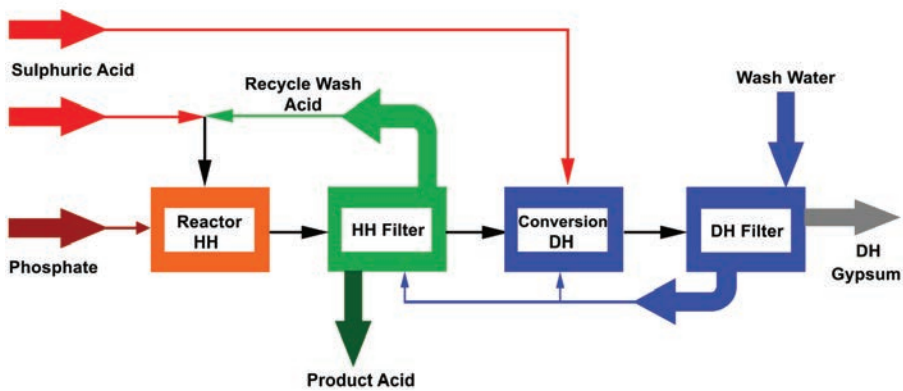


FIG. 76. The HDH method [65].

Appendix VI

COMPOSITION OF PHOSPHOGYPSUM

Data on the composition of phosphogypsum are given in Table 54 for the main chemical constituents, Table 55 for heavy metals and Table 56 for radionuclides. Some values have been rounded.

TABLE 54. MAIN CHEMICAL CONSTITUENTS OF PHOSPHOGYPSUM [48, 85, 133, 205, 209, 217, 325–330]

	Concentration (%)	
	Minimum	Maximum
CaO	24	34
SO ₄	48	58
SiO ₂	0.5	18
Na ₂ O	0.12	10
C (organic)	0.1	2.5
F	0.1	1.8
P ₂ O ₅	0.05	8
Al ₂ O ₃	0.05	0.6
Cl	0.035	0.045
MgO	0.01	0.54
Fe ₂ O ₃	0.01	0.25

TABLE 55. HEAVY METALS AND RARE EARTH ELEMENTS IN PHOSPHOGYPSUM [48, 74, 75, 77, 80, 137–139, 208, 219, 316, 325–327, 331, 332]

Element	Concentration (ppm)	
	Minimum	Maximum ^a
Ti	26	470
V	2	40 (190)
Cr	1.6	75 (594)
Mn	3.5	20
Co	0.05	2.3
Ni	1.7	250
Cu	2	195 (508)
Zn	4	315 (351)
As	1.0	42
Se	0.5	75 (249)
Sr	10	1118 (1606)
Y	2	156
Zr	10	110 ^b (398)
Mo	1	16
Ag	0.4	5 (73)
Cd	0.8 ^c	40
Ba	20	236 (810)
Hg	0.005	10
Pb	0.5	16 (73)
Th	0.4	4 (75)
U	0.5	13.8 (19)
La	42	90 (419)
Ce	21	143 (425)
Nd	30	67 (352)
Sm	5	13 (60)
Eu	1.1	3 (15)
Yb	2.1	3.2 (21)
Lu	0.3	0.4 (2)

^a Values in parentheses are maximum values reported for the fine fraction (<20 µm) [138, 139].

^b A value of 700 ppm was reported for phosphogypsum of igneous origin [48].

^c It is reported that, by adapting the parameters of the sulphuric acid digestion process, the cadmium concentration in the phosphogypsum can be reduced to less than 0.5 ppm, although this is offset by a higher cadmium concentration in the phosphoric acid [85].

TABLE 56. RADIOACTIVITY IN PHOSPHOGYPSUM (BY COUNTRY)

Location of phosphogypsum	Phosphate rock source		Activity concentration (Bq/g)							Reference
	Origin	Type	²³⁸ U	²³⁰ Th	²²⁶ Ra	²¹⁰ Pb	²¹⁰ Po	²³² Th	²²⁸ Ra	²²⁸ Th
Australia		Sedimentary	0.5		0.5			0.01		[333]
Belgium					0.44			<0.01		
Brazil	Brazil	Igneous			<0.004-0.67	0.05-0.89	0.05-0.68	0.01-0.18		[75]
Canada (Alberta)	Idaho	Sedimentary			0.9					[334]
Egypt	Egypt	Sedimentary	0.13		0.41			0.019		[50]
Finland					0.18			0.012		[50]
France			0.015		0.44			0.003		[50]
Germany		Sedimentary	—		0.60			<0.005		[50]
Hungary	Syrian Arab Republic	Sedimentary	—		1.1				0.07	[335]
India	Morocco	Sedimentary	0.17 (0.14-0.21)		0.82 (0.45-0.94)					[74]
Italy (Gela) ^a		Sedimentary			0.41-0.42					[323]
Netherlands		Sedimentary	0.05		0.9-1.25					[48, 87]
Nordic countries		Sedimentary			0.15-0.6	≤0.2	≤0.2	0.06		[48]
South Africa	South Africa	Igneous	0.07 (0.05-0.07)		0.11 (0.09-0.12)	<LLD ^b	<LLD	0.33 (0.13-0.59)	0.41 (0.35-0.5)	0.50 (0.24-0.63)
South Africa	Togo and South Africa	25% sedimentary 75% igneous	0.01-0.08		0.08-0.33	0.08-0.33	0.08-0.33	0.01-0.17	0.01-0.21	[48]

TABLE 56. RADIOACTIVITY IN PHOSPHOGYPSUM (BY COUNTRY) (cont.)

Location of phosphogypsum	Phosphate rock source		Activity concentration (Bq/g)							Reference
	Origin	Type	²³⁸ U	²³⁰ Th	²²⁶ Ra	²¹⁰ Pb	²¹⁰ Po	²³² Th	²²⁸ Ra	²²⁸ Th
Spain		Sedimentary	0.02–0.2		0.17–0.6	0.16–0.8	0.17–0.8	0.01–0.02		[48, 185]
Sweden	Russian Federation (Kola)	Igneous			0.02			0.06		[336]
United Republic of Tanzania	United Republic of Tanzania	Sedimentary	0.09	1.05	3.2			0.1	0.15	[49]
Tunisia (Sfax)	Tunisia (Sfax)		0.04–0.07		0.20–0.22			0.01–0.02		[219]
UK			0.13		0.63–0.78			0.01–0.02		[50]
USA (Florida)	Central Florida	Sedimentary	0.08–0.2	0.1–2.9	0.3–2.1	1.3–1.4	1–1.5	0.004–0.05	0.001	[16, 337–340]
USA (Florida)	Northern Florida	Sedimentary	0.005		0.50–0.55					[47]
USA			0.20		1.22–1.48			0.01		[50]
Former Yugoslavia		Sedimentary			0.4					[312]

^a Pa-234m: <0.01–0.025; Pb-214: 0.29–0.31; Bi-214: 0.25–0.27; Pb-212, Bi-212: 0.02.

^b LLD: lower limit of detection.

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Annex I

ASSESSMENT OF THE SOLUBILITY OF AIRBORNE DUST PARTICLES

I-1. INTRODUCTION

Radioactive particles deposited in the respiratory tract are removed by three main routes:

- (i) Absorption into the blood;
- (ii) Transport to the gastrointestinal tract;
- (iii) Transport to regional lymph nodes.

Absorption into the blood involves the dissociation of particles and the uptake into blood of soluble substances and material dissociated from particles. The rate of particle dissolution in lung fluids is a crucial factor in determining the absorption rate. In the absence of specific data on absorption rates, default values are specified by the International Commission on Radiological Protection (ICRP) for the three general lung solubility classes of fast (F), medium (M) and slow (S) [I-1].

When conducting a dose assessment, the assignment of an appropriate solubility class tends to be based on conservative assumptions, leading to the likelihood of the dose being overestimated. This problem can be avoided by directly measuring the solubility of inhaled radioactive particles. In vivo measurements in humans are the most reliable source of data, but such data may be unavailable or insufficient, especially for the inhalation of airborne dust particles containing radionuclides of natural origin. As an alternative method, in vitro dissolution tests have been developed and used as research tools to estimate the solubility of particles. In the study reported in Ref. [I-2], and summarized in this annex, dissolution fractions and dissolution rates were determined for several key radionuclides of the ^{238}U decay series contained within airborne dust particles generated in phosphate fertilizer production plants. Measurements were made using a simulated lung fluid in an in vitro dissolution system.

I-2. ASSESSMENT METHOD

Samples of settled dust, aerosol particles and bulk products originating from the phosphate industry in central Florida, USA, were employed for solubility testing. Bulk products are produced via a dry granulation process using

phosphoric acid as the feedstock. Dust originates from ungranulated products or small fragments of bulk products, which can be easily suspended as aerosols and subsequently settled. Since the granulator area is located inside a building, there is little possibility of airborne contaminants other than phosphate products. Therefore, the main components of the three types of dissolution test sample are likely to be similar. The sample materials comprised monoammonium phosphate (MAP) and diammonium phosphate (DAP).

The sizes of settled dust samples were found to be widely distributed, ranging from less than 1 μm to greater than 100 μm . The particle inhalability generally decreases with increasing particle size [I-1]. A typical upper size limit for suspended particles is 100 μm [I-3]. Large particles are seldom inhaled and, thus, contribute little to the committed effective dose. Therefore, the large particles were removed from settled dust with a 76 μm sieve prior to conducting the dissolution tests.

The particle size would be expected to influence the dissolution rate because of its relationship to the particle surface area — smaller particles would dissolve more rapidly than larger particles because a larger proportion of the particle mass is available for reaction by being close to the surface [I-4, I-5]. Samples of airborne particles smaller than 10 μm and samples of bulk products (MAP and DAP, with granule diameters of approximately 3 mm) were additionally tested for any potential size effect on particle solubility in the lung. The airborne dust samples were collected at the granulator area at two phosphate processing plants, using a PM₁₀ high volume sampler (Sierra-Andersen, Model 1200) at a flow rate of 1130 L/min for 3 d. Particles collected on quartz fibre filters were mechanically detached for dissolution testing.

Various types of in vitro dissolution technique have been used in previous studies [I-4], including:

- (i) Flow systems;
- (ii) Static systems;
- (iii) Batch methods.

The radionuclide mass concentration in phosphate particles is rather low. For example, the mass fraction of uranium in MAP and DAP ranges from 0.014 to 0.025% [I-6]. For dissolution techniques (i) and (ii), there is a lower limit on the applicable mass of target material. Therefore, dissolution technique (iii) — the batch method — was selected in order to increase the quantity of particles and, thus, increase the radionuclide concentrations in solution for analysis.

In previous studies [I-7, I-8], serum ultrafiltrate (SUF) had proved successful as a simulated lung fluid and was, therefore, chosen for this investigation. The SUF was prepared according to the procedures reported in those earlier studies and was

used in conjunction with the batch method. Samples of material weighing 5 g were suspended in 200 mL of SUF in a flask, which was immersed in a water bath at a controlled temperature of 37°C. For the DAP samples, the pH of the stirred suspension was maintained within the range 7.3–7.4. For the MAP samples, the high fractional dissolution of the material caused the pH to decrease to 5.6–5.8 during the first day. After extracting the solution following that first day, the pH could subsequently be controlled within the range 7.3–7.4 by passing a mixture of 5% CO₂ and 95% air through the solution at a flow rate of 200–1000 mL/min. Leachate samples were collected initially after one day and periodically thereafter for a maximum of 50–85 d. To collect the leachate sample, the entire suspension was first passed through a 0.5 µm filter membrane. After separation of the dissolved fraction, the remaining undissolved particles were washed with 20 mL of SUF and the mixture passed through the same membrane. The filtrate was then passed through a 0.1 µm filter membrane. This double filtration method significantly reduced the possibility of leachate contamination by undissolved particles, which would have resulted in an overestimation of the dissolution rate. The double filtered leachate samples were reserved for subsequent analysis. The undissolved particles were resuspended in 200 mL of fresh SUF for the next leaching and filtration step.

The sample residues obtained from the dissolution tests were dissolved using a mixture of HF and HNO₃ [I–9]. Approximately 40 mg of residues were placed into Savillex screw-top Teflon vials and 0.5 mL of optima grade concentrated HF and 2.5 mL of optima grade concentrated HNO₃ were added. After placing the vials in an oven at 100°C for 24 h, the samples were evaporated to dryness on a hotplate. Then, 3 mL of optima grade concentrated HNO₃ doped with HCl were added to the samples, the vials heated on the hotplate for 24 h and then evaporated once again. The final residues were redissolved in 4 mL of 5% HNO₃ and diluted (about 2000 times) in preparation for analysis.

The solubilities of uranium, thorium and lead in the particles were characterized by measuring their isotope concentrations in the leachates and residues. The measurements were performed by high resolution inductively coupled plasma mass spectrometry (Thermo Electron Corp., Finnigan Element 2). The use of inductively coupled plasma mass spectrometry for health physics studies has increased in recent years owing to its high sensitivity and rapid procedure [I–10] to [I–13]. The intensities of the isotopes were measured at medium resolution. The measuring equipment was calibrated using gravimetrically prepared uranium, thorium and lead calibration standards. The greatest contributor to worker inhalation dose in the Florida phosphate industry is ²³⁰Th, followed by ²³⁴U and ²³⁸U, respectively. Other radionuclides in the ²³⁸U series make trivial contributions to worker doses owing to either their relatively low inhalation dose coefficients (²³⁴Th and ²¹⁰Pb) or their low activity concentrations in MAP and DAP aerosol particles (²²⁶Ra and ²¹⁰Po). Although the activity concentrations of ²³⁴U,

^{230}Th and ^{210}Pb in the SUF were comparable to that of ^{238}U , their mass concentrations were too low to measure by mass spectroscopy as their half-lives are short in comparison to that of ^{238}U . The mass concentrations in the SUF were highest for ^{238}U among the uranium isotopes, for ^{232}Th among the thorium isotopes, and for ^{208}Pb among the lead isotopes. Consequently, the solubilities of uranium, thorium and lead were determined from direct measurement of ^{238}U , ^{232}Th and ^{208}Pb .

Since SUF contains background levels of ^{232}Th , the concentrations of ^{232}Th in most leachate samples were below the detection limit — the mean, median, and maximum values of the detection limit were 0.89 ± 0.36 , 1.03 and 1.15 mg/L, respectively. In such situations, the concentration of ^{232}Th was taken to be the maximum value of the detection limit. This conservative approach was taken in the light of the fact that an increased blood absorption of ^{230}Th will result in a corresponding increase in the worker effective dose.

The remaining mass fraction at each extraction time step was calculated using the following expression:

$$\text{Remaining fraction} = \frac{M_T - \sum_i M_i}{M_T} \quad (\text{I-1})$$

where M_T is the original mass of phosphate ions, ^{238}U , ^{232}Th or ^{208}Pb in the particle sample, and M_i is dissolved mass at each extraction. M_T was estimated as the sum of the cumulative masses measured in the leachate for all extraction steps and the final residual mass at the end of the dissolution test. Dissolution kinetics were expressed as the sum of two exponential functions as given in the lung clearance model described in Ref. [I-1]:

$$\text{Remaining fraction} = f_r e^{-s_r t} + f_s e^{-s_s t} \quad (\text{I-2})$$

where f_r and s_r are the dissolution fraction and rate constant for the rapid dissolution component, respectively, f_s and s_s are the corresponding values for the slow dissolution component, and t is the elapsed time [I-4]. Values of f_r , f_s and s_s were determined by means of a least squares analysis using SigmaPlot version 8.0 (SPSS, Inc.) [I-7]. Since the first leachate samples were collected only after one day, the solubility after shorter time periods (for instance, 10 min) was not directly measurable. The ICRP default value of 100 d^{-1} [I-1] was, thus, assigned as the rapid dissolution rate, s_r . A similar approach was adopted in Ref. [I-7].

It was postulated that the lung solubilities of radionuclides contained in the airborne particles of phosphate product are governed mainly by their chemical forms in the particles. The measurements showed that there was no statistically

significant correlation between the dissolution rate and the product type or particle size. Since the majority of the surrounding phosphate matrix in the particle dissolved very rapidly, particle size did not appear to influence the solubility to any great extent.

I-3. RESULTS

The results of the investigation are shown in Fig. I-1. While the majority of the phosphate (the main component of the inhaled particle) dissolved rapidly in the simulated lung fluid, the dissolution of uranium, thorium and lead was generally less rapid. Between 3 and 14% of the ^{238}U in the particles dissolved rapidly in the simulated lung fluid, while the remaining fraction dissolved with a half-time of 91–315 d. The dissolution kinetics for ^{238}U were noted to be close to, but slightly slower than, those of materials in lung solubility class M in the lung clearance model described in Ref. [I-1]. For ^{232}Th , less than 1.4% of the radioactivity dissolved rapidly in the simulated lung fluid, with the remaining fraction dissolving with a half-time of more than 866 d. Solubility data for ^{208}Pb displayed a wide sample-to-sample variation. Between 3 and 41% of the ^{208}Pb dissolved rapidly, while the remainder dissolved more slowly with a half-time of 38–866 d. It was concluded that, for the purposes of radiation protection of workers in Florida phosphate processing plants, the data supported the selection of lung solubility class M for uranium and lead and class S for thorium.

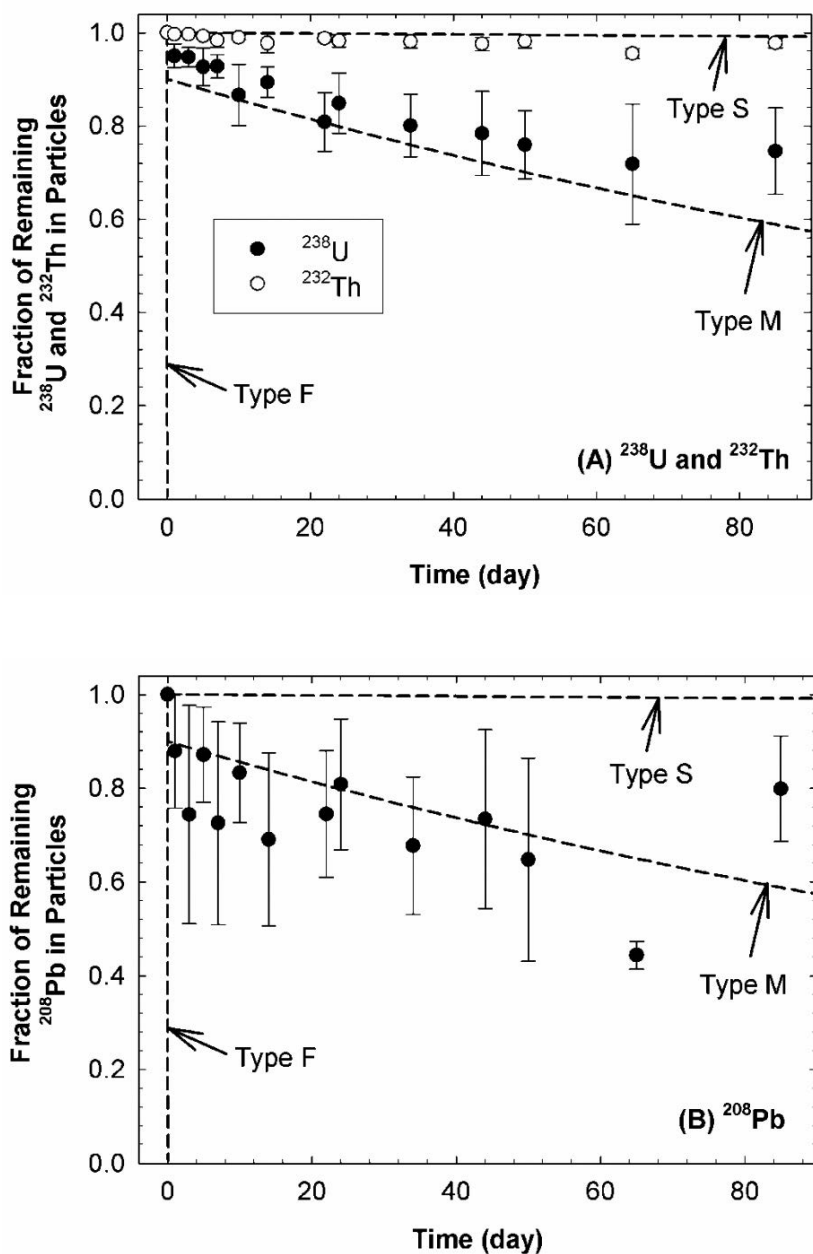


FIG I-1. Fractions of residual ^{238}U , ^{232}Th and ^{208}Pb in particles as a function of residence time in SUF simulated lung fluid. (A) ^{238}U and ^{232}Th ; (B) ^{208}Pb . Residual fractions for lung solubility classes S, M and F given in Ref. [I-1] are shown for purposes of comparison.

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Annex II

REMEDIATION OF COASTAL AND MARINE PHOSPHATE RESIDUE DEPOSITS: THE TAPARURA PROJECT AT SFAX, TUNISIA

II-1. TUNISIAN PHOSPHATE DEPOSITS

Tunisia's phosphate deposits are found in the north-east of the country, as well as further south. Of these, the most significant are located in the Gafsa basin in the south-central region. In 2010, the Compagnie des Phosphates de Gafsa produced 7.6 million t of phosphate rock from seven open-pit mines and one underground mine, making Tunisia the world's fifth largest producer. Phosphate rock and phosphate products (phosphoric acid, triple superphosphate (TSP), diammonium phosphate (DAP) and dicalcium phosphate (DCP)) together comprise Tunisia's primary export and are sold to 50 countries in five continents.

II-2. MINING AND PRODUCTION

Compagnie des Phosphates de Gafsa supplies approximately 80% of its phosphate rock production to the Groupe Chimique Tunisien, which operates several phosphoric acid plants. The remaining 20% of its production is exported through the port of Sfax. Groupe Chimique Tunisien has the capacity to produce more than 700 000 t/a of phosphoric acid, 1 million t/a of TSP, 600 000 t/a of DAP, 300 000 t/a of nitrogen-phosphate-potash and 100 000 t/a of monoammonium phosphate (MAP).

Groupe Chimique Tunisien owns four industrial production centres located in Sfax and M'dhilla (for TSP), Gabès (for phosphoric acid, DAP and DCP) and Skhira (for phosphoric acid). Approximately 800 000 t of TSP is produced annually at the Sfax and M'dhilla sites.

II-3. PHOSPHATE INDUSTRY ACTIVITIES AT THE CITY OF SFAX

The city of Sfax is located on the Gulf of Gabès, 270 km southeast of Tunis, and has a population of 340 000 (2005). It is the capital of the Sfax Governorate and is a leading centre of industry and commerce. Sfax is the largest port in Tunisia, handling the export of both phosphate rock and phosphate products.

Rock for export is transported by rail to the docks from the Metlaoui and Jebel M'dhilla mining areas.

The Sfax plant, which commenced production in 1952, was the first phosphate rock processing facility in Tunisia. It was also the birthplace of the multi-tank processing technology known as SIAPE, named after the company Société Industrielle d'Acide Phosphorique et d'Engrais that first developed it. SIAPE is now part of Groupe Chimique Tunisien. This method was designed to handle low grade phosphate ores. It was implemented at the phosphoric acid and TSP plants in Gabes, M'dhilla and Skhira.

The Sfax harbour facility was the location of an industrial area which included a phosphate plant that commenced operation in 1964. Phosphogypsum and other residues were discharged directly on to the beaches and into shallow offshore areas (the latter being, in effect, a 'dilute and disperse' management option), resulting in the accumulation of a large, square phosphogypsum stack close to the harbour and town (see Figs II-1 and II-2). As the stack increased in size, protective sea walls were constructed to confine the material and prevent erosion. The phosphogypsum residue contained low levels of metals, such as cadmium, arsenic and nickel, as well as radionuclides of the uranium decay series and, to a lesser extent, the thorium decay series. The average ^{238}U and ^{226}Ra concentrations in the Sfax phosphogypsum residues are at the lower end of the ranges reported worldwide. The ^{226}Ra activity concentration is approximately 0.4 Bq/g. The beaches were closed and swimming was forbidden in 1978 owing to the pollution arising from the phosphogypsum stack. The plant itself was closed in 1991. The stack, which covered an area of approximately 50 ha and reached a height of up to 8 m above sea level, was surrounded by a crusty layer of phosphogypsum ('plaque') with an area of 90 ha and a depth of up to 3 m.

Public exposure from operating phosphoric acid and fertilizer plants can occur through the inhalation of radon gas released from phosphogypsum stacks and through the migration of radionuclides into groundwater and surface water bodies, including the sea. Previous studies [II-1, II-2] have shown that the discharge of phosphogypsum into surface water bodies can result in significantly elevated levels of radionuclides, such as ^{210}Po in water, sediments and biota. Exposures are estimated to be in the range 2–10 $\mu\text{Sv/a}$ [II-3], with maximum values of up to 150 $\mu\text{Sv/a}$ [II-4]. The highest values occur where there are discharges to marine water and freshwater, resulting in the contamination of fish and shellfish used as local foodstuffs.



FIG. II-1. Satellite image of the Sfax phosphogypsum stack, harbour and town before the start of remediation work.

II-4. OBJECTIVE OF THE REMEDIATION PROJECT

The Taparura project at the Sfax site was divided into two main phases:

- (i) Identification and remediation of the contaminated areas and recovery of land from the sea;
- (ii) Development of the area and construction of a new urban centre.



FIG. II-2. Enlarged view of the Sfax phosphogypsum stack before the start of remediation work.

The project was initiated to remove the contaminated materials on the land and in the sea, to consolidate these residues into a designed central containment, to restore the beach facilities close to the town and to reclaim additional land from the sea for urban expansion and tourism. Remediation work on the project began in April 2006 and was carried out over a period of 28 months. The first project phase, involving the removal of contaminated material from the sea and on land, was completed by 2008. The recovered contaminated material was consolidated into an engineered structure and a cover layer was subsequently



FIG. II-3. Various stages of progress with the remediation project.

added. Revegetation of the cover layer began in 2009. The project entered a two year guarantee period in June 2009, during which the remediated area was inspected and evaluated, with a variety of monitoring programmes (including radiation monitoring) being implemented. Aerial views of the site at various stages of project implementation are shown in Fig. II-3.

II-5. PROJECT MANAGEMENT

Project management was carried out by an autonomous government company Société d'Études et d'Aménagement des Côtes Nord de la Ville de Sfax under the supervision of the Ministry for Infrastructure and Housing. The work of the project was performed by a consortium of specialist companies from Belgium, France, Netherlands and Tunisia. The project, which cost €75 million, was funded through taxes and through loans from the European Investment Bank and financial institutions in Belgium and France.

II-6. DEVELOPMENT OF THE REMEDIATION PLAN

Several comprehensive studies were carried out to characterize the site and to determine the extent of the polluted areas and the quantities of materials to be

remediated and contained on-site [II-5 to II-7]. The polluted area was assessed on the land and in the shallow sea surrounding the phosphogypsum stack. The monitoring focused on a number of key heavy metals (nickel, copper, cadmium, lead and chromium) and arsenic. The pollutant reference levels used to define the area requiring remediation were derived from Dutch standards on environmental remediation and were related to ecological risk criteria.

Once the extent of the polluted areas and the quantities of contaminants had been defined, the project engineers investigated the remediation options and the technologies required to complete the project. A clear priority was to minimize the contaminated area, which required the removal of significant quantities of solids from land and sea. Another priority was the long term physical stability of the containment and the design technology required to minimize the transport of pollutants from the containment into the surrounding groundwater. The design studies considered a number of long term aspects, such as the physical integrity of the structure and the site, hydrological aspects, the potential for floods and coastal erosion.

The option selected involved excavating the contaminated material (from both land and sea) and, after dewatering, incorporating it into the original phosphogypsum stack. Work carried out on the stack included the reshaping of the slopes, the installation of a vertical barrier around the perimeter in order to create a stable confined area, the installation of a cover layer of uncontaminated sand and the application of a new topsoil layer.

II-7. MOVEMENT OF MATERIAL

Approximately 1.7 million m³ of various materials were excavated on land, including approximately 1.25 million m³ of phosphogypsum plaque that surrounded the original stack. The modification of the stack shape from a square to a circular geometry involved the movement of 0.787 million m³ of material, while a further 0.465 million m³ of contaminated sediment was dredged from the sea and incorporated into the stack. The use of specialized computer controlled geographic information system positioning technology was required to dredge the polluted material from the sea. The polluted materials were sampled before and after dredging to ensure that the required level of decontamination had been achieved. The wet polluted material was stockpiled and dewatered in a specially designated area on top of the existing stack.

Backfilling of the remediated areas and the creation of a new beach entailed the movement of approximately 8 million m³ of material. It was necessary to dredge approximately 7 million t of sand from an unpolluted area approximately 20 km from the site using trailer suction hopper dredges. Coastal protection was



FIG. II-4. View of the site during the relocation of the plaque layers to the remediated stack.

enhanced by the construction of seven breakwaters around the site. The remediated site and containment were further protected by the construction of ring dykes and flood channels (requiring the excavation of approximately 0.45 million m³ of material) to provide for flood control, to enable the dewatering of the consolidated phosphogypsum and to provide access to the remediated site.

Various activities involved in the movement of material are shown in Figs II-4 to II-7.

II-8. THE REMEDIATED STACK

The rectangular phosphogypsum stack was converted into a circular, terraced structure with a diameter of approximately 0.9 km, an area of 55 ha, a maximum height of 16 m and a 1 in 5 slope (see Fig. II-8). A layer of uncontaminated soil excavated from a site 20 km from Sfax was used to cap the 4 million t of material contained within the structure. The soil thickness varied from 0.8 m (on the top and terraces) to 2 m on the slopes. The design studies and modelling carried out prior to remediation indicated that a minimum thickness of 30 cm of uncontaminated cover was required to attenuate adequately the radon gas and gamma radiation emitted from the contained material. This criterion was



FIG. II-5. Removal of the plaque layers.



FIG. II-6. View of the site during the backfilling of the rehabilitated areas with uncontaminated sand.



FIG. II-7. Backfilling of the rehabilitated areas with uncontaminated sand.



FIG. II-8. Aerial view of the remediated site, with the remediated stack visible in the centre.



FIG. II-9. Construction of the concrete-HDPE water barrier around the remediated stack.

based on the assumption that permanent structures such as housing or offices would not be constructed on the top of the remediated stack.

The remediated stack is underlain by a sandy silt layer (the original beach). Beneath this, 7–9 m below the ground surface, is a thick layer of natural, consolidated red clay. The stack is surrounded by a barrier comprising vertical, interlocking, 3 mm thick high density polyethylene (HDPE) panels embedded in a bentonite and concrete foundation 2.8 km long, 0.6 m wide and 12 m deep (see Figs II-9 to II-11). This barrier prevents the lateral movement of polluted water from the remediated stack into the surrounding groundwater. The foundation of the circular barrier is embedded in the natural red clay layer to a depth of 2.5 m. The groundwater levels on either side of the lateral barrier are automatically monitored. The design of the remediated stack includes a number of boreholes for sampling and for measurement of groundwater levels.



FIG. II-10. Construction of the concrete-HDPE water barrier around the remediated stack.



FIG. II-11. The base of the remediated stack, with the concrete-HDPE water barrier visible in the foreground.

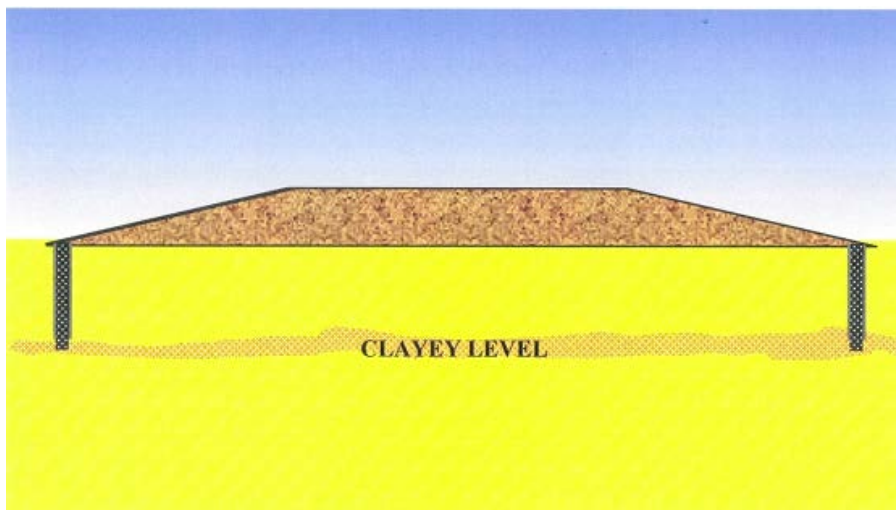


FIG. II-12. Simplified profile of the remediated stack, showing the underlying clay layer.

II-9. CONTROL OF SEEPAGE WATER

The clay layer beneath the remediated stack (see Fig. II-12) retards the downward movement of seepage water and purifies it by retaining a significant fraction of the heavy metal and radionuclide contents. The project engineers have estimated that the thickness of the clay is sufficient for this purification process to continue for several thousands of years.

The groundwater level below the remediated stack is constantly monitored by automatic systems. Water is pumped out automatically whenever the level approaches a height of 10 cm below that of the groundwater outside the water barrier. Seepage water beneath the remediated stack is collected and pumped through pipes into the flood control channel which then discharges into the harbour.

Prior to the remediation process (1994–1998), the seepage water had a high degree of acidity (pH4). Subsequently, the pH value rose towards neutrality and is now neutral. Analysis of the seepage water indicates that it contains elevated concentrations of phosphate and nitrate but very low levels of metal pollution.



FIG. II-13. Stormwater channel.

II-10. CONTROL OF THE QUALITY OF SURFACE WATER AND GROUNDWATER

The average annual precipitation in the area is approximately 250 mm and from time to time the Sfax area is subject to intense rainfall. In 1984 there was a 1 in 100 year storm resulting in severe flooding of the area. This impact was considered in the design of the project and the flood control canals were built to protect the remediated area and handle the large amount of surface runoff water anticipated from this type of event. The surface runoff is collected and directed into the flood control channel which discharges into the harbour (see Fig. II-13).

II-11. FINAL OUTCOME OF THE PROJECT

Up to 2011, 6 km of coastline had been restored. The project involved the creation of 6 km of beach and 420 ha of land for urban development (260 ha of remediated land and 160 ha of land recovered from the sea). The beach and landfill restorations have provided space for new recreational activities (e.g. beaches, parks and sports grounds), an educational, health and museum infrastructure and social housing programmes. Monitoring of the remediated areas will continue.

II-12. COMMUNICATION WITH THE PUBLIC

Communication with the public and stakeholder groups (e.g. individuals, community groups, regulatory bodies, universities and news media) was addressed at all stages of the project through a variety of mechanisms such as meetings, workshops, the internet, brochures and media communications. Throughout the project, the Centre Nationale de Radioprotection played a prominent role in addressing concerns about radiation issues.

II-13. RADIOLOGICAL SURVEYS AND ASSESSMENTS

The goal of remediation activities, such as those conducted as part of the Taparura project, is the timely and progressive reduction of the hazard and, eventually, if possible, the removal of regulatory control from the area without restrictions on future use [II-8, II-9]. In terms of IAEA safety standards, the remediation process should:

- (a) Reduce the doses received by exposed individuals or groups of individuals;
- (b) Avert doses to individuals or groups of individuals that are likely to arise in the future;
- (c) Prevent or reduce environmental impacts from the radionuclides present in the contaminated area.

Reductions in the doses received by individuals and the amelioration of environmental impacts can be achieved by actions applied to the source of contamination (e.g. isolation) or by actions to remove the source, to modify the exposure pathways or to reduce the numbers of individuals or other receptors exposed to radiation from the source.

From 1998 onwards, several comprehensive radiological surveys were carried out prior to, during and after the rehabilitation work to assess occupational and public exposures [II-10] to [II-16]. In addition, gamma radiation surveys were conducted to identify and to assess the contaminated areas. The surveys were conducted using portable instruments, fixed monitoring stations and integrating devices (thermoluminescent dosimeters and track etch devices) for gamma radiation, indoor and outdoor radon, radon progeny and airborne dust. After evaluation of the initial radiological assessments, the Centre Nationale de Radioprotection defined a level of public exposure of less than 1 mSv/a above background levels for the future use of the remediated site, which was in line with international recommendations and standards at that time [II-17] to [II-19].

The radiological assessments have demonstrated that, through the Taparura project, a reduction in the doses received by members of the public has been achieved by concentrating and containing the phosphogypsum residue in a central containment and backfilling the remediated areas with uncontaminated materials. The source is now confined to a small area of the site and the design of the remediated stack ensures that the migration of radioactivity into the environment remains within acceptable levels.

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