Uranium in phosphate fertilizer production

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Abstract. The production of fertilizers from natural phosphate ore can lead to the redistribution of uranium and other radionuclides in products, by-products and residues and, hence, to environmental impacts and increased radiation exposures.

Uranium and other radionuclides are mainly found in the process residue phosphogypsum and to a lesser degree in the final fertilizer products. The input of radionuclides of natural origin into the food chain via phosphate fertilizers appears to be of lesser concern. Because the radionuclide activity concentrations in most of the process materials are only slightly above levels in soil, the need for specific measures to control radiological hazards to individuals and the environment is very limited. In most cases, normal occupational health and environmental protection measures designed for non-radiological hazards will be sufficient to protect against radiological hazards as well.

Introduction

This paper summarizes the findings of recent reviews concerning radionuclides of natural origin in phosphate fertilizer production and associated radiation exposures. Uranium series and other radionuclides are ubiquitous in geological materials. The mining and processing of phosphate rock (phosphorite) to produce phosphate fertilizers, detergents, animal feeds, food additives, pharmaceuticals and other phosphorus-containing chemicals redistributes the uranium and other radionuclides (IAEA 2003).

The principal constituent of phosphate rock (or phosphorite) is the mineral apatite. The typical phosphate (P_2O_5) concentration of the rock is about 15-40%, with clay, sand, carbonate and other impurities present in varying quantities. Phosphate in mineable quantities is concentrated by sedimentary, igneous, weathering and biological processes (e.g. guano). Approximately 30 countries around the world produce significant quantities of phosphate rock. The principal suppliers of phosphate rock are the USA, Morocco, China and the Russian Federation, which together are responsible for about two thirds of total world production. Almost all phosphate rock is mined in open pit mines (IAEA 2003).

Uranium may be incorporated in sedimentary phosphorite ores through ionic substitution into the carbonate-fluoroapatitic crystals or by adsorption. Igneous phosphorite contains less uranium, but more thorium. Radionuclide concentrations in ores are given in Table 1.

Beneficiation

Generally, the starting material in production is beneficiated phosphate ore, referred to as marketable phosphate rock. During beneficiation, phosphate particles (mainly apatite and phosphorite) are separated out. Beneficiation can be simple, just screening or sieving the material and the overburden can be piled or returned to the mine; or more elaborate, including washing and flotation steps, producing phosphatic clay and sand tailings. Clay tailings are stored in large settling areas. Sand tailings are either returned to the mine and used as a backfill, used in the construction of clay-tailings retention dams or mixed with clay tailings to increase clay-tailings solids content and reduce settling times. In general, the beneficiation does not reduce the radionuclide concentration in the ore.

The phosphate ore is processed either by acid leaching, resulting in phosphoric acid, or by heat treatment in furnaces, leading to elemental phosphorus.

Table 1. Concentration of major radionuclides for different phosphate rocks (Roessler et al. 1979, Osmond et al. 1985, van Straaten 2002, Chernoff 2002, Makweba 1993, Banzi 2002, Othman 1992, CEC 2000, van der Westhuizen 2002).

Country	**Activity concentration [Bq/kg]**					
	^{238}U	**^{230}Th**	**^{226}Ra**	**^{232}Th**	**^{228}Ra**	**^{228}Th**
Sedimentary						
Central Florida	**750–3100**	**1300**	**700–3100**	**20**		
Northern Florida	**60–100**		**200–500**			
North Carolina	**600**					
China, Guangxhi	**600–1100**					
Morocco	**1000**					
Tanzania	**20–11 000**	**30–4500**	**5800**	**7–1100**	**500**	**150–1100**
Egypt, Nile Valley	**700**					
Syria	**750–1500**					
Igneous						
Russian Federation, Kola	**70**			**100**		
South Africa	**200**		**200**	**400**		**400**

Wet processing for phosphoric acid

The commercial production of phosphoric acid and of phosphatic application products proceeds by 'acidulation' with strong acids (H_2SO_4, HCl, HNO_3). The phosphoric acid is separated and further processed. Acidulation with sulphuric acid predominates world production (95%) and leads to the formation of 'phosphogypsum'. The gypsum precipitate can be easily separated from the raw phosphoric acid by filtration followed by washing. A neutralization step may be included. Unless the phosphoric acid is used for fertilizer production, it is further purified according to product requirements, e.g. by solvent extraction. The production of 1 t of phosphate (P_2O_5) results in the generation of approximately 4–5 t of phosphogypsum. A number of variations of the basic process (Fig. 1) are in use, mainly to reach higher yields and cleaner and more concentrated phosphoric acid.

Thermal processing for elemental phosphorus

Phosphate rock can be melted in a furnace (1400°C) with sand, iron oxide and coal for the reductive production of elemental phosphorus. Phosphorus and carbon monoxide are driven off as gases. The off-gases pass through dust collectors and then through water spray condensers, where the phosphorus is condensed and trapped in water. The residual solids in the furnace contain ferrophosphorus and calcium silicate, the slag. Slag is the principal residue while ferrophosphorus is considered to be a by-product.

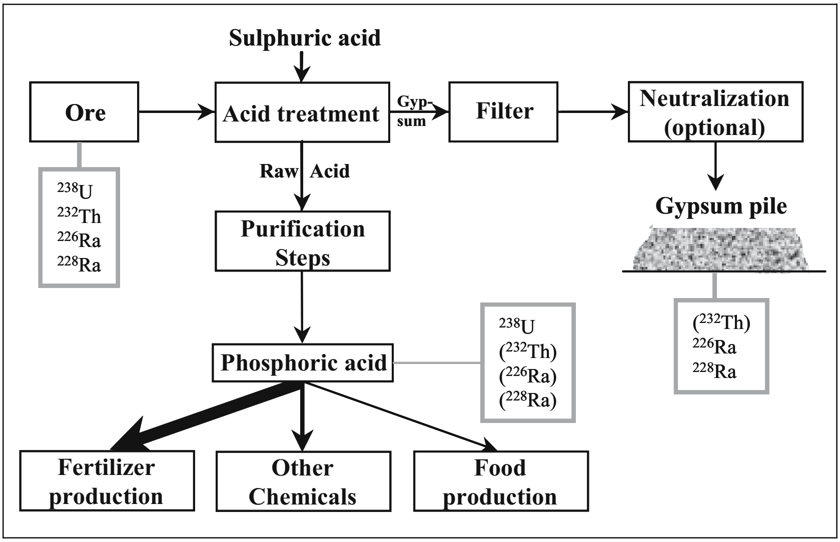

Fig. 1. Flow diagram of the sulphuric acid P-extraction process (IAEA 2003).

Radioactivity in products, by-products and residues

Phosphogypsum is the principal waste product generated by the wet process and arises as a slurry that is typically either deposited in piles (stacks) or discharged into rivers or the sea (Schmidt et al. 1995, World Bank 1998). Stacks may be covered with water to prevent radon emanation. In general, about 80% of the ^{226}Ra, 30% of the ^{232}Th and 14% of the ^{238}U is left in the phosphogypsum. Uranium and thorium become enriched in the fertilizer to about 150% of their original value (70% of the total U and Th budget) (Hull & Burnett 1969, Vandenhove et al. 2000). However, the amounts of radioactivity that are fractionated into gypsum vary significantly. The disposal of these wastes does not contribute significantly to the resulting radiation exposure. In the long term, radiological problems may arise, due to an unauthorized removal of wastes. Some countries have elaborate systems to manage these wastes. Management systems are likely to be dictated more by the non-radiological impacts (e.g. heavy metals) than by the radiological impacts.

The quantity of the slag from the thermal process amounts to 85% of the raw phosphate ore and contains the major fraction (93%) of ^{238}U and ^{226}Ra (Hull & Burnett 1969, Vandenhove et al. 2000). while part of the lead and polonium isotopes leave the oven with the gas stream due to their volatility. The electrostatic dust filter separates part of the radionuclide content from the gas stream, while polonium leaves the process mainly with the off-gas. The quantity of dust produced is about 1% of the raw phosphate ore. This may be recycled back into the process,

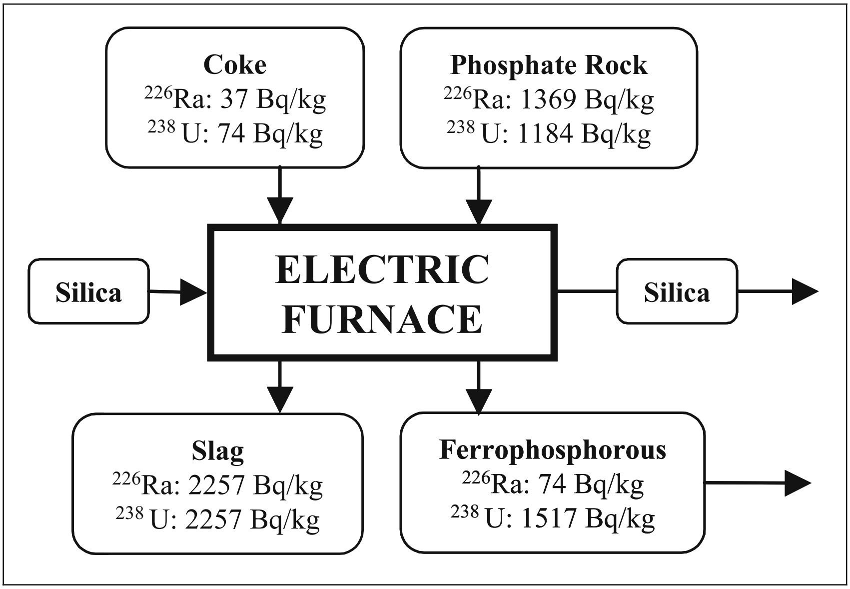

Fig. 2. Flow diagram and radioactivity balances for elemental phosphorous production (Hull and Burnett 1969).

but small amounts have to be purged from the system periodically to limit the build-up of high concentrations of organic matter and metals, which cause instability in the operation of the furnace. This recycling also causes a build-up of radionuclide concentrations. The dust purged from the system contains ^{210}Pb and ^{210}Po at activity concentrations of up to 1 000 000 Bq/kg (Erkens 1997), which can be immobilized with cement. A flow diagram for radioactivity balances in an American plant is given in Fig. 2.

Table 2 gives an overview of the radionuclide concentrations in residues from various process and of different origin.

The radioactivity content of fertilizers depends on the radionuclide content of the phosphate ore and on the method of production. Table 3 shows some values reported by Baetslé (1991) and extracted from a number of references. Fertilizers are generally depleted in ^{226}Ra content and display a U concentration pattern that is the result of either the dilution or the concentration effects of the fertilizer production process on the initial phosphate concentration in the ore. Although most of the U and Th remain in the fertilizer, fertilizer application does not significantly contribute to the general dose. Commercial calcium phosphates from furnace grade phosphoric acid do not contain any of the radionuclides present in natural phosphate.

Work carried out in Finland has shown that the annual contribution of ^{238}U contained in NPK fertilizers was about 0.25% of the total uranium naturally occurring in the top 10 cm of the soil. Similar results have been reported from Belgium. The long-term effects of phosphate fertilization on radioactivity have been studied in the United States. Triple superphosphate produced from Florida phosphate rock

Table 2. Radionuclide concentration in residues [Bq/kg], based on IAEA (2003) and references therein.

Country (Source)	^{226}Ra	^{238}U	^{210}Pb	^{210}Po	^{232}Th
Phosphogypsum					
USA S & C Florida	507-1358	41-366	577-1853	437-1765	11
N. Florida	270-599	22-451	348-551	355-566	
Europe	15-1700	500	1300	900	10
South Africa					
Local rock	45-48	64-73	76-132		205-284
Togo rock		17			61
Australia	280-350	10-24	320-440	150-360	4-7
Furnace slag					
USA	407-1517	444-2072	56	31	9-41
Europe	1000	1000-1500			
Ferrophosphorus					
USA	7-44	359-407	27-144	37	3
Calcined dust					
Europe			1 000 000		

and applied at the rate of 30 kg/ha of P during more than 50 years did not change the concentrations of U, Th, and Ra in corn leaves and grain, wheat grain and straw, or soybean leaves and bean, compared to non-fertilized plots (IFDC/UNIDO 1998).

Utilization of byproducts and residues

Since there are large quantities of phosphogypsum, the industry encourages its re-use in order to minimize the disposal problem; it is used as a fertilizer and soil conditioner, in road construction, and as building material (plasterboard and aggregate in concrete). In the USA, the primary use of phosphogypsum is in agriculture (1-2% of the generation), while the use in construction/building materials is now banned (USEPA 1990) due to the radon emanation. Other applications being considered include sulphur recovery from the gypsum, its introduction into municipal landfills to increase biological decomposition, construction of artificial reefs, and its conversion to calcium carbonate and ammonium sulphate (Florida 1996).

Phosphate slags find use as substitutes for valuable raw materials such as aggregate in asphalt manufacturing and as aggregate in concrete for making construction blocks etc. Slag has been incorporated in roofing shingles and, in the past, in the manufacture of ‘rockwool’ insulation. Phosphate slag is also used as railroad ballast and as stabilization material for stockyards (USEPA 1990). Forty percent of the phosphate slag produced in the USA is utilized in construction materials.

Environmental impacts of residues

The environmental impacts from (phosphate) fertilizer production has been summarized in a recent report (UNEP/UNIDO 1998). The release of radium into leachate and surface run-off from phosphogypsum piles is mainly determined by the solubility of the gypsum, which is generally very low. The dose resulting from ingestion of contaminated drinking water or food products is generally of no concern even for a member of a critical group living close to the pile. Exposure due to dust inhalation and radon are generally low due to the predominantly liquid stage of the gypsum stack. Furthermore, gypsum hardens when dry.

River dumping of gypsum may result in the contamination of the river embankments and increased exposure to the people living close by, mainly due to external exposure and exposure to radon (World Bank 1998).

Furnace slag is a glassy material containing the radioactivity in a vitrified matrix, resulting in limited leaching of radionuclides. In addition, the slag has a high carbonate content, which also reduces radionuclide solubility. However, USEPA’s

Report to Congress on Special Wastes (USEPA 1990) documents groundwater contamination at several phosphate slag waste management sites.

Application of international radiation protection standards

The International Basic Safety Standards for Protection against Ionizing Radiation and for the Safety of Radiation Sources (the BSS), jointly sponsored by six international organizations and published by the International Atomic Energy Agency (IAEA) in 1996, provide the basic requirements for the control of exposure to both artificial and natural sources of radiation (IAEA 1996). The BSS are supplemented by a number of IAEA Safety Guides. Although all raw materials contain radionuclides of natural origin, most do not warrant any form of regulation to control exposure to radiation, and the BSS apply only to those materials in which the radionuclide concentrations exceed the upper end of the worldwide distribution of activity concentrations in soil. This upper bound is deemed to be 1000 Bq/kg for uranium and thorium series radionuclides and 10 000 Bq/kg for potassium-40 (IAEA 2004a). It is usually unnecessary to regulate raw materials with activity concentrations below these values, and such materials can therefore be regarded as excluded from the scope of application of the BSS. For raw materials in which these levels are exceeded, regulatory control needs to be considered, but the regulatory body may still decide that the optimum regulatory option is not to apply regulatory requirements to the legal person responsible for the material, especially

Table 3. Radioactivity levels [Bq/kg] in phosphate products (Baetslé 1991, Vandenhove et al. 2000).

Products	^{238}U	^{226}Ra	^{232}Th
Phosphoric acid	**1200-1500**	**300**	
Normal superphosphate	**520-1100**	**110*-960**	**15-44**
Triple superphosphate	**800-2160**	**230*-800**	**44-48**
Mono ammonium phosphate	**2000**	**20**	**63**
Di-ammonium phosphate	**2300**	**210**	**<15**
Di-calcium phosphate		**740**	**<37**
PK	**410**	**370**	**<15**
NP	**920**	**310**	**<30**
NPK	**440-470**	**210-270**	**<15**

* low value for Former Soviet Union countries.

when the levels are exceeded by only a few times. In many cases, such a decision will be made by the regulatory body on a case by case basis and will take the form of an exemption. In several countries, regulatory requirements are applied only if the material is expected to give rise to doses to individuals exceeding 1 mSv in a year.

It can be seen from Tables 1–3 that most materials encountered in the phosphate industry either will qualify for exclusion or can be considered as candidates for exemption. Often, it is the presence of non-radiological hazards that will determine the need for occupational health or environmental protection measures, and such measures will usually have a beneficial effect on any radiological impacts. For instance, in the thermal processing of phosphate rock, normal industrial hygiene measures to control exposure to airborne dust will usually be sufficient to protect workers against the inhalation of radionuclides contained in the dust. Similarly, measures to limit the non-radiological impacts of phosphogypsum piles (e.g. leaching of heavy metals) will usually be sufficient to control any radiological impacts.

Measures for improvement and remediation

Three possible hazards from phosphogypsum waste have to be considered:

- the potential for releasing radium and non-radioactive contaminants into the environment;
- radon exhalation into the atmosphere, particularly in enclosed structures;
- the potential reuse of materials due to the loss of institutional control.

Options for remedial action on phosphogypsum piles can be guided by the technological state of the art in remediation of wastes from uranium mining and milling (IAEA 2002a,b, 2004b, in press), because the various hazards and requirements are quite similar. However, the radionuclide activity concentrations in phosphogypsum are typically one or two orders of magnitude lower, and this needs to taken into account when deciding upon the most appropriate course of action. In particular, the focus is likely to shift away from the radiological hazards more towards the non-radiological hazards.

There are processes, involving the concentration of the phosphoric acid and sedimentation, for the production of uranium in the form of ‘yellow cake’. However, the process is not economically viable at the present price of uranium (OECD/IAEA 2002).

Possible environmental benefits from efforts to reduce uranium and other radionuclide concentrations in fertilizer products would have to be weighed against environmental costs, such as increased concentrations in residues and higher energy consumption.

Conclusions

The main residue of concern from the production of phosphate fertilizers is the phosphogypsum, since uranium and other radionuclides are mainly found there and only to a lesser degree in the fertilizer products. Long-term stable solutions for the safe use or disposal of phosphogypsum will have to be designed in order to prevent environmental impacts (including non-radiological impacts such as those from heavy metals). The radionuclide input into the food chain via phosphate fertilizers appears to be of lesser concern. Most process materials in the production of phosphate fertilizers are borderline in terms of the applicability of international radiation protection standards, as the concentrations of radionuclides of natural origin are not very far above those found in soils worldwide. Radiological impacts on workers, members of the public and the environment will in most cases be adequately controlled by the application of normal industrial hygiene and environmental protection measures designed to protect against non-radiological hazards.

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