Radioactivity in the Phosphate Field: Actions Undertaken by IMPHOS

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Abstract. In order to prevent a potentially negative impact on the phosphate industry of the European Council Directive 96/29/Euratom, IMPHOS participated in several events where discussions were held on the issue of NORM and the consequences of the application of the Directive for the non-nuclear industries, including all the NORM symposia from September 1997 to May 2004. In addition, IMPHOS has undertaken actions to establish an ad hoc committee with members designated by member companies and to initiate a desktop study conducted by CEPN to review the implications of applying the Directive for the phosphate industry. This study is an important collection of data on radiological protection, including doses expected to be received by exposed individuals and monitoring considerations. The main conclusions of these actions are that the radioactivity in the phosphate industry is relatively insignificant, with the total annual exposure of a phosphate worker being less than three thousandths of the limit recommended by the ICRP.

1. Introduction

All raw materials contain traces of natural radioactivity. The main contributions to human exposure to ionizing radiation arise from natural sources, cosmic rays, the radionuclides in the Earth's crust and the natural radioactivity of the human body. The science of radiological protection, and national and international regulatory regimes, have evolved to ensure safety in the use of these sources of exposure.

In May 1996, The European Union issued Council Directive 96/29/Euratom that set limits on radioactivity concentration in naturally occurring radioactive material (NORM). In order to monitor the impact of the Directive on the phosphate sector, IMPHOS commissioned the Centre d'Etude sur l'Evaluation de la Protection dans le Domaine Nucléaire (CEPN), France, to undertake a study and participated in several events where discussions were held on the issue of NORM and the consequences of the application of the European Directive for the non-nuclear industries.

2. Radioactivity in phosphate rock and derivatives

Rock phosphate and its derivatives contain a number of elements, including impurities such as cadmium (Cd), nickel (Ni), chromium (Cr) and the radioactive elements uranium (U), thorium (Th) and their decay products. Rock phosphates are chemically processed more and more in the producer countries and directly exported as 54%P_2O_5 phosphoric acid to produce intermediate products, such as triple super phosphate and ammonium phosphates. Different processes are needed because of different rocks and gypsum disposal systems. The chemical reaction by the wet process is:

$$Ca_3(PO_4)_2 + 3H_2SO_4 \rightleftharpoons 2H_3PO_4 + 3CaSO_4$$

The insoluble calcium sulphate (phosphogypsum) is then separated from the phosphoric acid, usually by filtration.

Phosphate Fertilizers vary considerably from one product to another with regard to their radioactive material content, ranging over an order of magnitude (30–300 ppm weight). Table 1 illustrates some typical values of naturally occurring radioactivity in some phosphate rock. About 80% of the ^{226}Ra, 30% of the ^{232}Th and 14% of the ^{238}U is left in the gypsum.

3. Actions undertaken by IMPHOS

Radioactive elements in phosphates have attracted much interest, particularly when recovery of U from phosphates has an added value. IMPHOS has addressed the issue of phosphate radioactivity

since its creation. It has sponsored research on U recovery by ionic floatation at the University of Nancy. The research work was recognized by a granted patent. In order to survey the application of the new European Directive, IMPHOS contracted CEPN, France, to conduct a study on radioactivity issues in phosphate products and participated in several events where discussions were held on the issue of naturally occurring radioactive materials (NORM) and the consequences of the application of the European Directive for the non-nuclear industries.

TABLE 1. TYPICAL RADIOACTIVITY LEVELS IN PHOSPHATE ROCK

Origin	Activity concentration (Bq/kg)		
	^{238}U	^{226}Ra	^{232}Th
Florida	1 500	1 600	16
South Carolina	4 800	4 800	78
Morocco	1 700	1 700	30
China	150	150	25

3.1. Assessing radioactivity in phosphate mining and processing

Because of possible concerns over the radiation exposure that could result from the handling of radioactive materials and from the use or disposal of their wastes, the European Commission has supported a programme of work in this area over a number of years and has assembled a substantial body of information by means of contracts and contributions from experts. As protection against the effects of ionizing radiation, the Member States of the EU were previously subject to two Directives: 80/936/Euratom of July 1980 and 84/467/Euratom of September 1984. The new European Directive 96/29/Euratom, which was implemented on May 2000, is more restrictive than the previous Directives and provides a regulatory control system for the protection of the workers and the public from sources of ionizing radiation. However it does not necessarily apply to the exposure to natural radiation sources

In order to provide more background on the EU objectives, underlying principles and scope of application of the planned Directive, and a detailed method for the initial evaluation of the degree of annual exposure of workers from different phosphate industry activities, IMPHOS commissioned the CEPN, France, to undertake some work on *Modalities of Application of Title VII of the Directive 96/29 EURATOM to the Phosphate Industry: Analysis of the European Regulation and Presentation of a Method of Evaluation of Exposure*. The report constituted an important collection of data and information on the radiological protection system, with quantitative data on the range of doses that can be received by a person or by certain organs and tissues in particular, the permissible limits for certain exposed workers and the public, the classification of workplaces and work conditions, the monitoring of individuals who can be subject to internal radiation and the monitoring of exposure to contamination through skin. The study also provided updated information on the application of the Directive in each EU Member State and the sectors of the industry to be considered in this application with particular attention to the phosphate industry.

During the introduction of the broad guidelines and major conclusions contained in the report, the author underlined the need for the phosphate industry to undertake specific communication campaigns in order to provide relevant and credible data and information on the subject and to avoid as much as possible any misunderstandings and confusion, and thus any negative reactions and attitudes of the general public.

3.2. Symposia and meetings

IMPHOS participated in several events where discussions were held on the issue of NORM, extending from NORM I held in 1997 to NORM IV in 2004.

NORM I

The NORM I symposium was held in Amsterdam from 8-10 September 1997 and covered the following topics: the phosphate industry, metal production, the refractories, abrasives and ceramics industry, the TiO_2 pigment industry, the oil and gas industry and the coal and fly-ash industry.

In the phosphate industry, radioactivity is particularly located in phosphogypsum, dust (phosphate rock or fertilizers), sludge and scales. The concentrations of natural radionuclides in phosphate ore vary from 100 to about 5000 Bq/kg and are dominated by the contribution of the ^{238}U decay series. Igneous phosphate rock contains much less uranium but higher concentration of ^{232}Th. Phosphoric acid produced from rock phosphate via the wet process retains roughly 60% of the most highly soluble radionuclides (U, Th). Indeed, 80% of the radium existing in phosphate rock is retained by the phosphogypsum, with a ^{226}Ra activity concentration of 900–1300 Bq/kg.

In the thermal process, phosphate ore is crushed, mixed with silica and coke and calcined at a temperature up to 1500°C in an electrical furnace to produce elemental phosphorus P4. Because of the high temperature of process, about 95% of the relatively volatile radionuclides are released to the process air, giving typical concentrations of 50–500 Bq/g of ^{210}Pb and ^{210}Po in dusts.

The concentrations of radionuclides in fertilizers vary widely, in part due to the different chemical compositions of fertilizers and also due to the raw material used in their production.

NORM II

IMPHOS participated in the International Symposium NORM II held in Germany on 10–13 November 1998. The symposium was organized in five sessions. Each one of the sessions dealt with a specific aspect of NORM: measurement and monitoring, exposure of the workers and the public, experience of the industry, waste management, legislative and regulatory aspects. The conclusions and recommendations of the symposium can be summarized as follows:

- The intended mode of application of the European standard remains ambiguous and requires the EU to establish guidelines for the application of the standard at the level of each Member State of the EU in the shortest time.
- In collaboration with scientists and legislators, the industry should assume leadership in the discussion of the Directive with the EU,
- The application of the new Directive should necessarily take into account the additional cost associated with decontamination.
- Methods of determination of radioactivity were not well defined and no consensus was reached on the meaning of ‘natural’ radioactivity in the current clearance criteria.
- The term radioactivity is rather ambiguous and needs to be better clarified.
- Often, the dose rate calculations are based on conservative assumptions that lead to unrealistically high results.
- The industry fears that, if regulations are passed, they will increase the production costs which might lead to a loss of competitiveness regarding other countries.
- There is a need for clear international harmonized policy on how to process the large volumes of contaminated industrial waste and scrap.
- There is a need for developing guidelines by the EU on the transfer of the Directive into national laws.

NORM III

IMPHOS participated in a meeting of the scientific Committee connected with the third symposium of NORM held in Brussels in May 2001. IMPHOS was part of the committee that selected the papers to be presented or submitted as papers or posters. The selected papers for presentation were scheduled in the different sessions, and figured under the eight different topics of the symposium, which were as

follows: regulatory aspects, mineral processing, the mineral salts, coal, radon in the working place, wastes, the environment, and the scrap and construction material industry. As a result, the phosphate industry does not figure among the industries on the list. In fact, only one Greek paper dealt directly with the phosphate industry. It was a paper from the University of Thessalonika that looked at the atmospheric fallout from phosphate processing plant and its impact on the surrounding environment.

NORM IV

IMPHOS participated in the NORM IV symposium held in Poland in May 2004. With regard to phosphates, the symposium included coverage of igneous rock phosphate (from volcanic origin), which is more radioactive than sedimentary phosphate — this is due to the elevated level of ^{232}Th in the igneous rock, and discussed the possible uses and management of phosphogypsum and the scaling found in different parts of the phosphoric acid plant. The discussions during the previous NORM symposia show that the radioactivity of phosphate rock and phosphate fertilizers would seem to pose no risks to the environment.

IAEA meeting in Vienna in May, 2002

IMPHOS participated in a meeting held by the IAEA in Vienna in May 2002 on the topic *The Extent of Environmental Contamination by Naturally Occurring Radioactive Material (NORM) and Relevant Abatement Measures*. The IAEA prepared a technical document (TECDOC) that reviews all the sources of naturally occurring radioactivity. On phosphates, the input from IMPHOS was particularly to provide relevant information about radioactivity in phosphates and phosphate fertilizers.

International Consultation Meeting in Florida

IMPHOS attended an international consultation meeting on the future of phosphate and phosphate related products, held at the conference centre of the Florida Institute of Phosphate Research (FIPR) in Bartow, Florida on October 3–4 2006. This meeting was organized in association with the IAEA, the Nuclear Energy Agency (NEA) of the Organization for Economic Cooperation and Development (OECD) and other partners. A major focus of the meeting was on safety and risk assessment. The meeting discussed the fundamental changes occurring in the phosphate industry that are being driven by structural transformations in the world economy, changing attitudes to risk, renewed concerns about strategic raw materials and increased concern for the environment and waste reduction. The meeting also explored options for responding to the likely consequences of these changes, including possible collaborative work plans. During this event, it was noted that, phosphate is a limited resource that cannot be synthetically produced, and phosphogypsum is a co-product of phosphoric acid production that has some unique properties and advantages over other forms of gypsum and can be used as a fertilizer, a soil conditioner, backfill for road construction, a construction material for the production of plasterboard, and cement aggregate.

4. Some developments and considerations on the issue of radioactivity in phosphates.

The solutions ensuing from the studies, symposia and meetings to overcome the radioactivity problem of NORM are the following:

- Radioactive wastes should be, in this way, diluted in the liquid ecosystem. Thus, from a radioactivity viewpoint, it is more appropriate to dilute radioactive waste than to dispose of them into piles.
- Spreading of waste with relatively low concentration of natural radioactivity over the land may not, or may only with a low percentage, increase the original radiation field. Phosphogypsum can be widely used as a beneficial soil amendment. Uptake of crops grown on such amended soils is still acceptable.
- Some PK fertilizers which contain radioactive materials slightly above the exemption levels do not affect the natural radioactivity at soil level while spread all over.

- There is a tendency to reuse naturally occurring radioactive materials as a way to decrease the volume of waste. Phosphogypsum and sludge from phosphate industry are widely used for road construction and wall board plaster.

Radioactivity in phosphate mining and processing is found mainly in:

- Phosphate ore dust emission during mining, beneficiation, chemical processing, handling, and storage,
- Processing of wastes, in particular phosphogypsum which concentrates radium,
- Sludge and scaling in the whole equipment used in wet process phosphoric acid production.

In order to prevent problems with radioactivity in phosphate industries, IMPHOS is called upon to take a pragmatic strategy. Hence, the following plan was proposed:

1) To undertake a campaign of information about the impact of radioactivity from the phosphate industry towards member companies.
2) To institute a think-tank with member companies' participation in order to lay down an 'IMPHOS Position', which can be promoted by the IMPHOS Secretariat at regional level (EU), to the International Committee on Radiological Protection (ICPR), to institutions that develop regulatory standards, as well as other involved institutions such as EFMA, IFA and PPI.
3) To follow-up news pertaining to the matter at hand by developing an information network involving EU and international bodies such as ICPR, directly concerned with their research activities or decision making.
4) To carry out a self-auditing of radioactivity levels in member companies' facilities according to a pre-agreed programme based on conventional tests and procedures.

With respect to phosphogypsum, which receives on average 40% of the radionuclides present in the phosphate rock — a percentage that involves particularly the less soluble portion of radionuclides, i.e. radium and polonium — the problem of radioactivity increases particularly from the exhalation of ^{222}Rn that has relatively a short half-life and does not pose a significant health hazard.

Finally, regarding phosphate fertilizers, the problem of radioactivity is raised at two levels:

a) At the storage level where fertilizers continue to exhale ^{222}Rn in the surrounding atmosphere. The sufficient means to reduce the effect of ^{222}Rn is to practice adequate ventilation in warehouses.
b) At the level of fertilizer use where radioactive elements are thought to get into plants, and at the current level of knowledge, it seems that there is little evidence to show that the passage of radionuclides in the food chain starts with phosphate fertilizer use even if P were to be applied at a high rate.

5. Conclusion

The main conclusions and recommendations are:

– The natural radioactivity of phosphate rock is still lower than that of some soil and radioactive material in the atmosphere.
– The total annual exposure of phosphate workers to radioactive material in a closed workspace is lower than three thousandths of the admissible threshold recommended by the International Commission on Radiological Protection.
– Several studies have shown that, in general, the radioactivity in the phosphate industry is insignificant compared with other industry sectors.
– This is why the scientific community pays less and less attention to the phosphate industry.

– The nuclear scientific community estimates that the issue of hazards due to NORM and particularly phosphate rock is considered as not important enough to warrant undertaking any efforts to solve it.

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