Inhalation doses and regulatory policy in wet-acid processing of sedimentary phosphate rock

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Abstract. The wet-acid method of phosphoric acid and fertilizer production exposes workers to both mists and dusts containing naturally occurring radioactive material (NORM). The relative contributions of the uranium and thorium series and activity concentrations of their members depend primarily upon the source of the processed ore. The wet-acid process is the prevalent method used by the industry and varies little worldwide. Consequently, similar facilities can and perhaps should compare monitoring results by scaling to the activity concentrations of the processed ores. A global effort to characterize and benchmark activity concentrations in ores, products, and by-products would be extremely advantageous in fostering good management practices for the phosphate industry. Early studies focused on external doses to workers involved in phosphoric acid filtration and maintenance of the filtration assemblies. As more comprehensive dose assessments emerged, the inhalation component was examined using high-volume samplers, gross activity counting methods, and a simple model of the respiratory tract for dose conversion. Inhalation doses came under more scrutiny with the advent of the revised human respiratory tract model (HRTM), computer programs for its implementation (LUDEP and IMBA), improved air sampling techniques, and an emphasis on scenario-based probabilistic dose assessments. Without adequate parameter data, probabilistic dose assessments can generate possible, although not probable, doses that approach or exceed some regulatory limits. These recent developments highlight the importance of determining the sensitivity of inhalation dose estimates to the model parameters such as airborne particle size distributions and their solubilities in lung fluid. It is also important to carefully consider these data during ALARA review and when forming regulatory policies regarding the need for respiratory protection programmes and administrative or engineering controls, thus lowering the risk of over-regulation.

1. Introduction

Phosphate rock processing is a broad subject and a full discussion of the industry is beyond the scope of this paper. Thermal processing, processing of igneous rock, and the lesser-applied technologies, such as digestion of rock with nitric acid, will not be discussed. Wet-acid processing of sedimentary phosphate rock using the dihydrate method is the dominant production mode for phosphoric acid and its derivative fertilizers. Sulphuric acid is reacted with phosphate rock concentrate slurry to produce phosphoric acid and phosphogypsum according to the reaction:

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \text{ --> } 3CaSO_4 \cdot 2H_2O + H_3PO_4$$
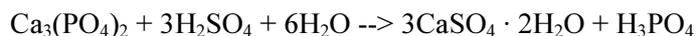
Sedimentary phosphate rock contains NORM of the uranium, thorium and actinium series. The activity concentrations of the members of these series vary with the source of the ore. The rock itself also varies in mineral structure and constituents. There are, however, some identifiable trends in the distribution of radionuclides during processing.

1.1 Distribution of radionuclides

A proper inhalation dose assessment requires knowledge of the distribution of radionuclides through the process that converts phosphate rock to phosphoric acid and dry fertilizer products. If only gross activity measurements are taken, knowledge of the process radiochemistry reduces assumptions that must be employed, and thereby reduces conservatism in the final dose estimate. Some of the more important elements are discussed below.
- **Uranium** – It has been known for decades that most of the uranium goes with the phosphoric acid as soluble salts. Phosphoric acid is produced when concentrated phosphate rock slurry is

mixed with sulphuric acid. The efficiency of the acid digestion depends on the rocks surface area available for attack, the residence time in the attack tank, mixing, and other factors. Consequently, a small amount of rock will pass through undigested along with the uranium it contains. This uranium goes into the phosphogypsum byproduct. Many factors, such as oxidizing conditions and overall P_2O_5 recovery, are involved in uranium partitioning, so there is no definitive correlation between rock content and acid and phosphogypsum contents.

- **Radium** – Most of the radium goes with the phosphogypsum (primarily $CaSO_4$), since radium is a divalent cation like calcium. A small fraction of phosphogypsum and other impurities gets through the filtration process and into the phosphoric acid product. The acid is clarified in large settling tanks to remove much of these contaminants.

- **Lead** – There are contradictory statements in the published literature. Some report that all lead goes with the phosphogypsum, while one reports that most ^{210}Pb goes with the acid [1]. If the latter is correct, the activity concentration of ^{210}Pb in phosphogypsum is determined by ingrowth from [222]Rn. That is not likely. It would take considerable time (about 100 years) to establish a [226]Ra/^{210}Pb ratio of unity, which can be found in fresh gypsum [2]. Also, a TVA-TFI study [3] showed that most of the lead goes with the gypsum, probably as lead sulphate. $PbSO_4$ is quite insoluble.

- **Polonium** – One study indicated that over 99% of [210]Po goes with the phosphogypsum [4]. This is also supported by isotopic ratios in the phosphogypsum [2]. Mazzilli et al. [5] reported that 78% of the [210]Po goes to the phosphogypsum in Brazilian wet-acid facilities.

- **Thorium** – Thorium forms sparingly soluble salts with hydroxides, fluoride, and phosphate. Sulphate compounds are relatively soluble. Complexes with phosphate, sulphate, and fluoride should dominate. Partitioning is variable as with uranium, but most of the thorium goes with the acid [2]. These authors were surprised to find that only 25% of the thorium reports to the gypsum. Other authors [5] reported higher than expected thorium fractionation to gypsum (80%) and attribute thorium distribution to variability in chemical processes.

1.2 Phosphoric acid and phosphogypsum byproduct

Dissolved uranium is carried by the phosphoric acid as uranyl phosphate, sulphate, and fluoride complexes. Uranium has tetravalent and hexavalent forms. The tetravalent form in the rock feed is oxidized to U^{6+} and the uranyl ions mainly complex with phosphates. Research funded by the Florida Institute of Phosphate Research has shown that solids suspended in collected samples and sediments produced during storage contained gypsum; the alkali fluosilicates, Na_2SiF_6 and $NaKSiF_6$; chukhrovite, $Ca_4SO_4SiAlF_{13} \cdot nH_2O$; and a complex iron phosphate, $Fe_3(NH_4,K,H)H_8(PO_4)_6 \cdot 6H_2O$. Data evaluations suggested the latter compound was mostly, but not exclusively, present in the ammonium form. There is a long list of other possible compounds [6]. All of these can be expected, especially gypsum, to have radionuclide substitutions. The primary ones to be expected are radium sulphate, lead sulphate, lead disulphate, polonium disulphate, and thorium disulphate. Also, chukhrovite is notorious for having high radium content as radium substitutes for the four calcium ions.

The radionuclides known or suspected to go with the gypsum can form fluorides, oxides, hydrides, and sulphides. Sulphides are not a problem when processing Florida rock, because arsenic precipitates the sulphides. Other sources of rock, e.g., North Carolina, will give a sulphide smell. For examples of other compounds, consider polonium and radium. Since the reaction takes place in air, there will be some polonium dioxide. There may even be some fluorides of polonium (likely to be volatile and decompose rapidly). There can also be various less common combinations of ions. Since fluorine is present, there could be a small amount of radium fluoride. Some phosphate makes it through the digestion process, so there may also be $Ra_3(PO_4)_2$.

There was at least one attempt to separate radioactive materials from the phosphogypsum using a cyclone. A higher proportion of the radioactivity is found in the fine fraction. This makes sense because the radium and calcium do not actually co-crystallize due to differences in solubility of the sulphates (calcium sulphate is soluble and radium sulphate is highly insoluble), difference in ionic

radii between Ca and Ra, and differences in the crystalline structures of the sulphates [7]. That means that the radium in phosphogypsum should be in the form of small crystals of radium sulphate, not bound to other crystals. The coarse fraction is gypsum mixed with some undigested rock, also containing radioactivity including radium from the rock, but the overall mixture should be a lower activity concentration than the fine fraction. The main problem is that not enough radioactive material can be removed to make a meaningful difference.

Uranium is present in phosphate rock primarily as U^{4+} (40 to 91%, mean of 65%) presumed to be followed by U^{6+} as the remainder [8]. It is also assumed that U^{4+} substitutes for Ca^{2+} in the apatite structure because of their nearly identical ionic radii. However, there are very few U atoms available for substitution (1 U: >25,000 Ca) and there are other more plentiful substitute ions available, e.g., sodium and magnesium. During acidulation, ferrous iron readily reduces U^{6+} to U^{4+}. The reduction is also catalyzed by fluoride ion from the rock [4]. A small amount of U^{4+} reports to phosphogypsum for three major reasons: a) phosphogypsum coats unreacted rock particles containing uranium, b) due to some substitution of uranium in the crystal lattice of the phosphogypsum, and c) acid losses containing uranium phosphate to the phosphogypsum. Small amounts of uranium may be present in phosphogypsum in the form of the uranyl ion (UO_2^{2+}) contained within the residual phosphoric acid which remains after filtration and transport to the stack. U^{4+} may adsorb on the surface of phosphogypsum as UO_2HPO_4 or UO_2^{2+} may substitute for two Ca^{2+} ions on the surface of the crystal lattice [9].

1.3 Reaction of Phosphoric Acid with Ammonia

Diammonium phosphate (DAP) and monoammonium phosphate (MAP) are the major granulated products formed by the reaction of ammonium hydroxide with phosphoric acid. The chemical formula for DAP is $(NH_4)_2HPO_4$. Certainly, you would expect the oxides of uranium to form. There are a lot of possibilities with uranium, and with plenty of phosphate ions available, combinations of the two should be plentiful. One could speculate that uranium diphosphate would be the dominant species, but a literature search did not reveal an answer.

With granulated triple superphosphate the situation is even more complex. In that case, the rock concentrate is reacted with phosphoric acid to yield the original beneficiated mineral (e.g., francolite) with more uranium added in and a multitude of possible chemical combinations.

2. Global radioactivity database

The wet-acid process is used throughout the world with only minor variations of any consequence to radionuclide distributions. This means that one could roughly scale the expected activity concentrations and inhalation hazards to the input rock source. This would save significant resources that may be unnecessarily devoted to monitoring programs, respiratory protection programs with dubious benefits, and unwarranted regulatory restrictions.

Published data on the radionuclide and metals contents of worldwide phosphate rock, wet acid process products, and phosphogypsum are highly variable in time of sampling, analysis methods, and parameters chosen for analysis. At best, the existing data can yield only a partial picture of the current international market. In order to establish a concurrent, coordinated and consistent database, an internationally funded program would obtain samples of rock from currently active mining sites, and products and phosphogypsum from active processing sites. Rock samples would be correlated to the processing sites where they are used. A model structure for such a program already exists. Rothamsted Research (UK) has been collecting, storing and analyzing soil, fertilizer and crop samples from their experimental plots for one and a half centuries. Not only have these samples served their original purposes, but also have revealed trends, e.g., pollution and radioactive fallout, unforeseen by the scientists who collected them so long ago. Nevertheless, they had the foresight to realize that other uses for the samples would develop.

The phosphate industry and regulators should follow their lead. Essentially, use a well-vetted sampling protocol, use the best analysis equipment available, follow rigorous QA/QC, and store the samples for future research. For the first time, all major global rock production and processing sites would be analyzed for a comprehensive set of radionuclides, metals, and other parameters of interest according to a rigorous set of protocols. In this way, the data set will be complete and uncertainties stemming from differences in analytical techniques and sample handling will be avoided. All laboratories will use the same set of handling protocols and analysis techniques. Quality Assurance/Quality Control will be maintained using chain of custody, and cross-checking with standards and a statistically reliable subset of samples. Both the database and the analytical protocols used in its development will become the new benchmark for the Twenty-first Century global phosphate industry and samples will be stored and categorized as in the Rothamsted model.

3. Inhalation dose characterization

Once benchmark data are in place, whether making a rough estimate of projected doses or a rigorous site-specific inhalation dose assessment, certain parameters must be known or assumed (with justification). Inhalation dose assessment techniques have greatly improved over the last half-century. In past decades, phosphate industry inhalation dose assessments were conducted by taking high-volume air samples in the workplace that were analyzed for gross activity. Many assumptions were applied to estimate doses to workers. With the advent of cascade impactor sampling, high-resolution spectroscopy, the revised human respiratory tract model and computer applications, inhalation doses can be estimated with fewer conservative assumptions and less uncertainty. Consequently, inhalation dose estimates tend to be lower using the newer techniques and measurements of sensitive parameters.

Olszewska-Wasiolek [10] assessed radioactive materials in the workplace using Ge(Li) gamma spectroscopy, and alpha spectroscopy (for ^{238}U and ^{210}Po only). The most important radionuclides, as ranked by Annual Limit on Intake (ALI) for all three natural decay series, were considered for the phosphate dust inhalation assessment. Unpublished data (unknown methodology) gave a mean particle diameter of 1.6 microns, so a default AMAD of one micron was used for all particles. The range of dust loading was reported as 3.0 – 13.5 mg/m^3. Activity concentrations of dust samples were not measured, and were estimated based on raw materials. Committed effective doses due to phosphate dust inhalation ranged from 2.85 - 5.60 mSv/a. The lack of sufficient data for sensitive inhalation dose parameters required application of conservative assumptions and likely resulted in the overestimation of dose. This conclusion was also expressed by the author of the study.

The equipment and techniques necessary to gather data on the missing parameters are expensive and complex. Birky et al. [11] experienced the same difficulties and also used a default AMAD, made radionuclide activity concentration estimates based on gross radioactivity collected on filters in conjunction with bulk material measurements, and made conservative assumptions about particle solubilities in lung fluids. Results were published as dose distributions. The most probable doses for individual workers were:

> <0.05mSv/a for those moving rock concentrate

> <0.02mSv/a in phosphoric acid production

> <0.05mSv/a in dry product areas

> <0.8mSv/a in product shipping and storage.

Use of uncertainty analysis techniques invariably compounds individual parameter uncertainties on occasion to produce very high potential doses, which are nevertheless highly unlikely in reality. For that reason, the displayed range of possible doses for workers who move dry materials in shipping and storage areas was up to 3.5mSv/a. These authors also recognized that the inhalation doses were very likely to be overestimated and recommended a more targeted follow-up study to gather data on the unknown parameters.

The first follow-up study was completed in 2005 [13] accompanied by four related publications authored by Kim et al. [14–17]. Measured parameters included airborne particle size distributions, particle densities, particle shapes, particle chemistries, and radionuclide activity concentrations.

Solubility of particles in lung fluid was not examined during the first follow-up study pending the outcome of a sensitivity analysis for that parameter. The sensitivity analysis proved that the inhalation dose is extremely sensitive to this parameter, so further studies were conducted [18–19].

Dust samples were collected at areas identified in the first comprehensive study [11]. These areas included the granulation area for dry products, dry products storage warehouse, and shipping operations. An example of the dry products storage area is shown in Fig. 1. Particle mass concentration was found to increase with increasing particle size at the majority of the plants and operational areas.

FIG. 1. Dry products storage area.

Sampled aerosol particles appear as spheroids or rough spherical fragments under scanning electron microscopy using samples from all seven cascade impactor stages. The main elemental components of large-sized and medium-sized particles are similar to those in bulk dry product. For small-sized particles, the fraction of phosphorus is small in comparison to elemental impurities such as silicon and sulphur. The density of products and particles are 1.6–1.7 g/cm^3. The ^{238}U, ^{226}Ra, and ^{210}Pb radioactivity concentrations in bulk dry product and settled dust from central Florida range from 2.33–4.15 Bq/g, 0.0296–0.0555 Bq/g, and 0.248–0.333 Bq/g, respectively. No significant differences in the concentrations of ^{238}U and ^{226}Ra were found between dry product, settled dust, and airborne particles. ^{210}Pb is, however, highly concentrated in airborne particles up to 3.2 Bq/g, probably due to attachment of ambient airborne radon decay products on workplace airborne particles.

Under the least conservative assumptions of blood absorption rates, all worker exposures are less than 1 mSv/a. In contrast, the most conservative assumptions yield worker effective doses in excess of 1 mSv/a for some 44%, 31%, and 15% of individual effective dose assessments at granulator, storage, and shipping areas, respectively. The study thus demonstrates the importance of facility- and area-specific particle solubility data in effective dose assessments.

Lung fluid solubility of uranium, thorium, and lead in phosphate product particles was determined using an *in vitro* dissolution test using serum ultrafiltrate (SUF) lung fluid stimulant [20] at the physiological pH of 7.2–7.4 consistent with lung lining extracellular fluid. The solubility data and other aerosol information were then used for individualized effective dose assessments at six phosphate facilities. Dissolution testing showed that the majority of phosphate, the main component

of the inhaled aerosol particle, was dissolved rapidly in the lung fluids. Uranium, thorium, and lead however, did not dissolve as rapidly as did the surrounding matrix (Fig. 2). From 3–14% of the ^{238}U in NORM aerosols dissolves rapidly in the lung fluids, with the remaining fraction dissolves with a half-time of 91–315 days. The dissolution kinetics for ^{238}U in phosphate processing NORM aerosols were noted to be close to but slightly slower than that of Type M materials in the ICRP 66 clearance model. For ^{232}Th, less than 1.4% of the radioactivity is dissolved rapidly within the lung fluids, while the remaining fraction dissolves with a half-time of more than 866 days. Selection of Type S is thus recommended for dose assessments in radiation protection. Lung fluid solubility data for ^{208}Pb displayed a wide sample-to-sample variation. Of the ^{208}Pb, 3–41% is dissolved rapidly, while the remainder dissolves more slowly, with a half-time of 38–866 days. No noticeable correlations were found between radionuclide solubility and the product type or particle size. The data support the selections of ICRP 66 (1994) Type M for uranium and lead and Type S for thorium as adequate for the purpose of effective dose assessment to workers in these phosphate processing facilities. Inhalation effective doses were calculated using the most current human respiratory tract model (HRTM).
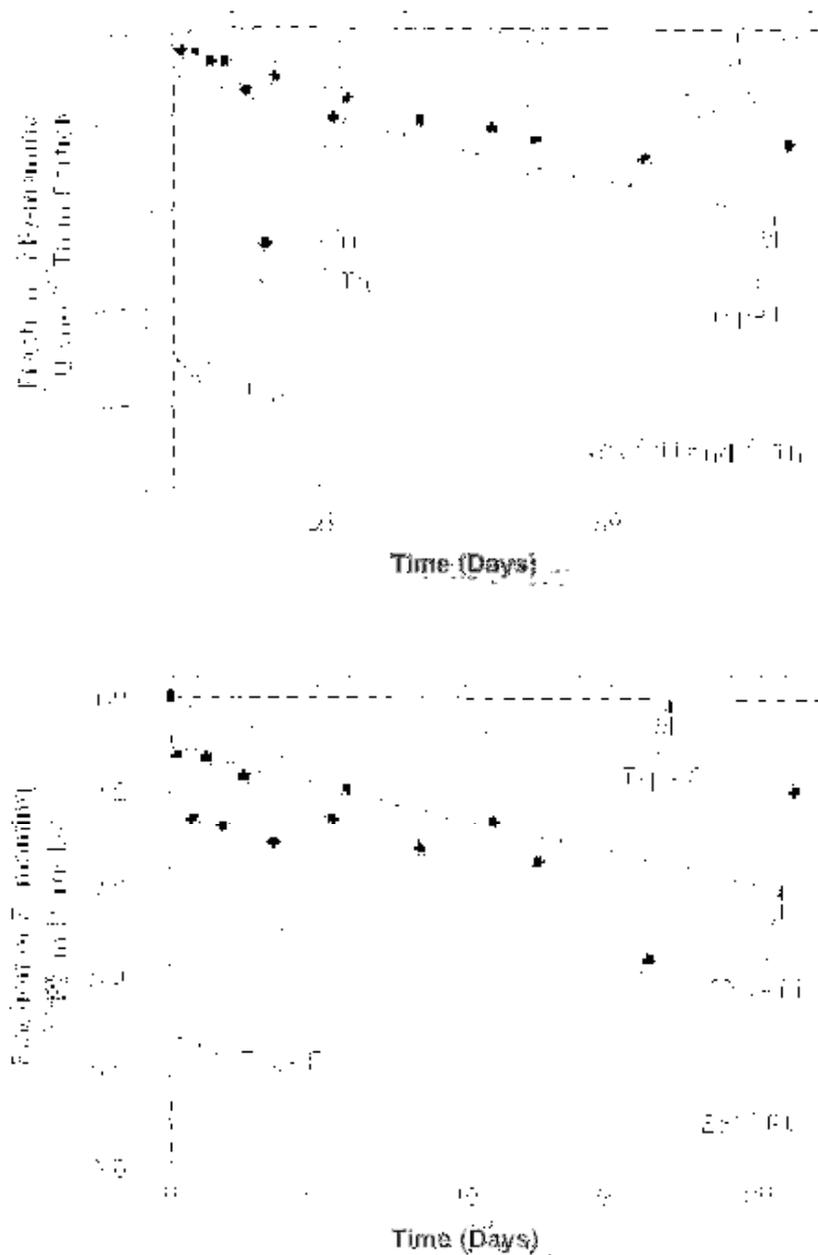

FIG. 2. Fraction of remaining ^{238}U, ^{232}Th, and ^{208}Pb in particles as a function of time in serum ultrafiltrate (SUF): (A) ^{238}U and ^{232}Th and (B) ^{208}Pb. Retentions of default absorption type materials in ICPR 66 HRTM are depicted for comparison

4. Regulatory policy

The IAEA BSS [21] provides the framework for the protection of NORM industry workers. In conjunction with published scientific articles, IAEA Safety Reports describing processes and good practices, some basic site-specific data, and a "graded" approach [22] to regulation, worker protection is assured without undue expense on the part of industry. The BSS is in place and some NORM issues will be readdressed in the next version, important inhalation dose parameters have been recently measured and published as discussed herein, and an IAEA Safety Report for the phosphate industry is in draft. The main missing components for effective and harmonized worldwide regulation are the global radioactivity database described in this article, and the political will to cooperate.

At least three quarters of the sedimentary phosphate rocked mined in the world today contains less that 2 Bq/g of the individual members of the uranium and thorium series, and much is less than 1 Bq/g. Even at levels approaching 2 Bq/g the resulting inhalation doses are well below 1 mSv/a. Personnel monitoring programs persist at facilities throughout the world despite the fact that in many cases they achieve no practical benefit and would qualify for the lowest level of the graded approach, i.e. no regulation necessary.

It is important to carefully consider these data during ALARA review and when forming regulatory policies regarding the need for respiratory protection programs and administrative or engineering controls, thus lowering the risk of over-regulation.

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