Working with Ores Containing Naturally Occurring Radioactive Materials

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Introduction

A variety of ores and minerals that contain the naturally occurring radioactive material arising from the presence of thorium and uranium are processed in factories that have nothing to do with the nuclear power industry. These include phosphate rock, titanium dioxide bearing ores, rare earths and materials containing compounds of zirconium. This paper draws attention to the radiological protection problems associated with the use of these materials and their by-products with particular focus on keeping exposures as low as reasonably achievable (ALARA).

The materials

A list of the ores considered in this paper, together with typical activity concentrations, is given in Table 1. The activity concentrations can vary, sometimes quite widely, so the values given are only for guidance. Ores are, more often than not, subjected to purification processes before being made commercially available. Depending on the process, this may upset the equilibrium naturally present in the ore bed. The list is not exhaustive.

Table 1. Ores containing naturally occurring radioactive materials

Ore	Main constituent	Typical active concentrations ($kBq\ kg^{-1}$)	
		Thorium-232	Uranium-238
Phosphate rock	Calcium phosphate	0.1	1.5
Ilmenite	Iron titanium oxide	1	2
Rutile	Titanium dioxide	0.2	0.2
Rare earth concentrate	Cerium oxide	5	0.1
Baddeleyite	Zirconium oxide	1	10
Zircon	Zirconium silicate	0.6	3
Pyrochlore	Niobium oxide	80	10
Monazite	Cerium phosphate	300	40

The presence of radioactive materials in these ores can be detected with portable radiation monitoring equipment, especially when bulk material is present and with the possible exception of the rutile, ilmenite and phosphate rock, the ores pose a degree of external hazard. All of them pose a degree of internal hazard, particularly by inhalation.

In some cases the industrial processing of the ores causes some of the radioactive material to become concentrated in deposits and scales. In processes designed to remove impurities, radioactive materials tend to become concentrated in waste streams and in by-products; this is particularly true of the isotopes of radium. Polonium and, to a lesser extent, lead are concentrated in the fume from high temperature processes because of their volatility. Thus, materials are formed that are potentially more important from a radiological protection point of view than their sources. This is discussed more fully below.

The processes

Phosphate rock

This is the major commercial source of phosphoric acid and of phosphate-derived material such as fertilisers and detergents. Phosphoric acid is made by attacking the raw material with sulphuric acid. The by-product gypsum has radium contamination at similar concentrations to that in the phosphate rock. Uranium-238 tends either to stay in solution with the acid or be released with liquid effluent. The major radiological problem in this process is, however, from radium rich scales which form in parts of the process, such as in filters, tanks and pipework. The concentration of radium-226 can easily exceed 100 kBq kg^{-1} causing high levels of contamination and significant dose rates. Radiation exposures have been kept as low as reasonably achievable through isolation and containment, and the prudent use of protective clothing and good working practices.

European interest in this process has largely now waned as the tendency is for the ore producing country to process the rock and sell the phosphoric acid. The uranium content of the phosphoric acid may still be of concern from a waste disposal viewpoint.

Ilmenite and Rutile

These are the major sources of the pigment material titanium dioxide. Two processes are still operational within Europe. A sulphuric acid digestion is similar in principal to that described above for phosphate rock and has similar attendant problems of radium rich scales. Here, however, radium-226 concentration in excess of 300 kBq kg^{-1} have been found. Again, judicial use of personal protective clothing and good working practices combine to keep exposures low.

The second process is known as the Kroll process. In this, the purer rutile or ilmenites that have been concentrated by the removal of iron, are chlorinated at high temperatures. Fractional distillation is then used to collect titanium tetrachloride, from which a pure titanium dioxide can be made. The major waste streams have radioactive material that is slightly more concentrated than the feed stocks. This process also gives rise to radium rich scales, but at concentrations less than the two previous examples and much more localised. Similar techniques are successful in keeping exposures low.

Rare earth concentrate

The major use of this material is in glass polishing where it is much more effective than the traditional rouge. It is also used as an additive in the glass industry. In both cases the processing is simple and by-products and waste streams are of little radiological consequence. Inhalation of dust is the main source of exposure. The manufacturing process of the glass polishing compound is reasonably continuous and dust exposure can be chronic. Even where the plant is designed to minimise dust by automatic transfer systems, airborne dust levels have been of concern. The methods for the introduction of the raw material into the plant and the packaging of the product have been especially problematical. Other spills contribute to the problems and the eagerness of the workers to get on with the job has sometimes led to their not wearing the breathing protection that they have been provided with and trained to use.

The industry is keen to find a material with a lower thorium content, partly to avoid the radiological protection problems but also because a traditional source is currently coming to an end. One very promising source from the Far East has been found with a thorium content some ten times less than that given in Table 1. Caution must however be exercised in these choices and the following experience is related to emphasise this. Seventeen one tonne bags of this source were obtained for trial processing. Sixteen of these gave analyses for thorium consistent with the low level mentioned above. One bag, however, had a material with a thorium content of 25 kBq kg^{-1}. Fortunately this was discovered when a high external gamma dose rate (20 _Sv h^{-1}) was found close to this bag before it was processed.

Because glass polishing normally requires small amounts of the material, exposures even under the sloppiest of conditions are very small. There is no UK experience of large-scale use though this is theoretically possible and would give rise to similar radiological problems to those in the manufacturing process.

Baddeleyite and Zircon

The excellent metallurgical properties of zirconium, plus the refractory and other properties of zirconia, make the processing of these materials much more widespread than those mentioned above. Processes include a high temperature treatment, chemical purification, manufacture of refractory bricks, nozzles and dielectric materials. The materials are also used in ceramic glazes and in high temperature casting.

To keep the issues in focus, what follows concentrates on the more important radiological protection aspects. Where bulk materials are stored an external gamma dose rate of about 2 _Sv h^{-1} and 6 _Sv h^{-1} will exist for zircon and baddeleyite, respectively. While these are not excessive, simple precautions such as segregation are appropriate to keep exposures as low as reasonable achievable.

When these materials are moved or otherwise manipulated there is a potential for dust levels to increase and for inhalation of radioactive material to be an issue. Control techniques typically include ventilation and local extraction to keep dust levels within manageable proportions. Experience to date indicates that this is not always totally effective and the use of respiratory protective equipment such a dust masks, respirators or powered face masks are necessary in some cases to keep exposures as low as reasonably achievable.

An interesting extra dimension is present when the material is heat treated, for this drives off the more volatile radioelements, polonium and lead in particular. These then tend to deposit in the cooler parts of effluent ducting and in bag houses or precipitators. Polonium-210 concentrations can exceed 600 kBq kg^{-1}. These deposits do not give rise to external dose rates but are a potential source of inhalation. The main problem, however, is disposal.

Finally the authors have recently become aware of a process involving the manufacture of high purity zirconium compounds from zircon sands. The radionuclides are mostly removed and appear in the liquid chemical effluent, usually at quite low concentrations. At one time, this effluent was passed through an ion exchange treatment plant and this gave rise to considerable concentration effects within the pipes and vessels of this plant. A sample from the bottom of a large acid tank had a radium-226 concentration of over 5000 kBq kg^{-1}. Dose rates of up to 400 _Sv h^{-1} were measured around the tank; in a nearby workshop a dose rate of 30 _Sv h^{-1} was measured. Fortunately internal exposure has not been an issue because the material was effectively sealed within the column. The decommissioning of the plant and the disposal of the waste are now the main issues.

Pyrochlore and monazite

These are briefly mentioned here out of historical interest because there are currently no UK factories using either of these materials. Their importance from a radiological point of view lies in the very much greater activity concentrations present in these materials than in those considered above. Because of this, external gamma dose rates can be relatively high and both inhalation and ingestion problems are much greater.

Others

There are many materials not mentioned above that are relatively rich in their activity content. Some of these, such as pitchblende, uraninite and davidite, are important sources of uranium for the nuclear industry. Their treatment is not considered further here except to say that the radiological issues will be similar to those encountered with pyrochlore and monazite. Materials may also be encountered where there is a slight enrichment of radioactive material. Some sources of bauxite provide an example of this.

Radioactive materials may also be found in the by-products of the processing of materials that themselves had elevated activity. Calcium chloride, a by-product of the phosphate industry, rare earth salts prepared from monazite (where the purification has been poor), a tantalum rich powder, a ferro-zirconium silicate are all examples of this. The further treatment of bulk quantities of these materials could give rise to further radiological consequences. The lesson to be learned from this is that vigilance must be exercised over source materials if ALARA is to be achieved.

Radiological issues

In the UK, work with radioactive materials has been subject to the Ionising Radiation Regulations 1985[(1)]. These Regulations have been deemed to apply to work with materials such as ores, where occupational exposures might exceed 5 mSv effective dose per year. Doses to workers have been found to be typically in the range 0–5 mSv per year, although in some cases annual doses have been 10 mSv or more per year[(2, 3, 4)]. Where doses have been high, internal exposure from the inhalation of dust has been the dominant exposure pathway.

As a consequence of the European Basic Safety Standards Directive[5], these regulations are to be revised[6] and the 5 mSv per year „application level“ will be reduced to 1 mSv per year. At the same time, adoption of the most recent ICRP dose coefficients for internal radiation exposure[7] will mean estimated radiation doses from the inhalation of dust will be substantially reduced – by up to factor of 10 or more in some cases.

Some of the practical effects of these changes are:

a) exposures from inhalation of dust, often the dominant exposure pathway in the past, are expected to be of a similar magnitude to those from external exposure, except where very high levels of airborne dust are present;

b) for many of the materials described, estimated annual doses from external radiation exceed 1 mSv per year if continuous exposure is assumed. Consequently, it is important that dose estimates are based on realistic assumptions regarding work patterns and occupancy Even then, it is expected that more use will be made of personal dosemeters (at least for trial periods) to assess external doses;

c) to date, measurements have indicated that radon concentrations have not reached significant levels, even where quite high concentrations of radium-226 are present. In future, however, relatively low levels of radon emanating from ores may be significant in terms of whether the work is subject to the revised regulations. The passive etched-track detectors (PADC or Cr-39) traditionally used for radon measurements may not be sensitive enough detect these low levels.

d) in trying to assess annual doses as low as 1 mSv per year from natural radionuclides, the level of background radiation is an important consideration. Representative background measurements of gamma dose rate and, in particular, *indoor* radon concentrations are required; and

e) exposure from ingestion of material is expected to remain an insignificant exposure route except where high activity concentrations, such as in radium rich scales, are encountered.

Processes currently subject to the Ionising Radiations Regulations 1985 will, therefore, need to re-assess the radiological hazard in light of the revised regulations. It is also expected that a number of processes currently exempted from the requirements of the regulations will need to assess whether this will still be the case in future. In both cases, increased attention to external exposure and radon emanation will be necessary.

Those processes that are subject to the regulations are expected to address the same requirements as practices involving artificial sources, including that of ALARA. In practice, a flexible approach to radiation protection is required which takes into account both the scale of the operation and the activity concentrations of the materials present, for example:

a) the materials with lower activity concentrations give rise to modest dose rates (typically a few microsieverts per hour) even at the surface. Dose restriction usually relies on discouraging access, for example by storing materials in mostly unoccupied areas. Physical barriers and warning signs are typically reserved for areas containing scales and other materials with greatly enhanced activity concentrations;

b) the control of inhalation doses in large ore processing facilities is based on the industrial hygiene principles that are applied to airborne dust in general. Engineering controls are the favoured option; working procedures and, finally, respiratory protective equipment being considered only where further engineering controls are not reasonably practicable;

c) the complete containment of material is often impractical, especially where large quantities of low activity concentration ores and minerals are involved. In such cases, spills and the spread of materials outside the area are often of no radiological significance, unless substantial and persistent airborne dust levels result. The usual radiological controls applied to „surface contamination“ only become meaningful where higher activity concentration materials are present; and

d) worker training and information is particularly important to support the introduction of local rules and explain the precautions therein.

Summary

1. This paper gives some indication of the variety of materials and an even wider variety of processes that involve natural radioactivity. The problems associated with radium scales demonstrate that vigilance is needed wherever there is large scale processing of feeds that contain even small concentrations of

radioactive materials. This is reinforced by the recent discovery of a process in which the concentration of radioactive material had gone unnoticed for many years.

2. The impending changes to UK regulations brought about by the implementation of the European Basic Safety Standards Directive will require that the occupational radiation exposures associated with the processes described will need to be re-assessed. It is expected that a number of processes that are currently exempt from the Regulations will need to reassess their position.

3. The changes in internal radiation dose coefficients will significantly reduce the importance of the dust inhalation pathway. Processes giving rise to worker doses of more than 1 mSv will be subject to the regulations. At this level of exposure, external radiation, dust inhalation, and inhalation of radon may all be significant pathways. Dose estimates based on realistic assumptions, together with an increased use of personal dosemeters (external radiation) and radon gas measurements to directly assess occupational exposures, are anticipated. In assessing these exposures, careful subtraction of natural background is an important consideration.

4. A flexible approach to the regulation of these processes, and to the ALARA principle in particular, is often required. The system of protection needs to be practical, taking into account both the activity concentration of the material and the scale of the process.

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