Chapter 6

Radioactive Wastes of Uranium Ores

6.1
Introduction

Uranium ores have the specific issue of radioactivity, and uranium mine wastes are invariably radioactive. This property differentiates uranium mine wastes from other mine waste types. For example, gold mine tailings contain cyanide, and the cyanide can be destroyed using natural, naturally enhanced or engineering techniques. Sulfidic wastes have the potential to oxidize, and oxidation of sulfidic wastes can be curtailed using covers. In contrast, the decay of radioactive isotopes and the associated release of radioactivity cannot be destroyed by chemical reactions, physical barriers or sophisticated engineering methods. Therefore, appropriate disposal and rehabilitation strategies of radioactive uranium mine wastes have to ensure that these wastes do not release radioactive substances into the environment and cause significant environmental harm.

The fundamental characteristics of uranium mine wastes are given in this chapter with a particular focus on radioactivity, uranium tailings, and the behaviour of uranium in mine waters. Some uranium ores contain abundant sulfides. The presence of these minerals in pit faces, underground workings, tailings, and waste rock piles may lead to sulfide oxidation and AMD. The principles of sulfide oxidation and AMD have already been presented in Chaps. 2 and 3. Sulfidic uranium mine wastes and their acidic waters may be characterized and treated with the same type of approaches used to characterize and treat sulfidic wastes and AMD waters.

6.2
Mineralogy and Geochemistry of Uranium

6.2.1
Uranium Ores

Uranium ore minerals can be classified as reduced and oxidized species. Reduced uranium minerals incorporate uranium as U^{4+} whereas oxidized species have uranium as U^{6+}. Uraninite (UO_{2+x}) is the most common reduced U^{4+} mineral species, and it is the main ore mineral in many uranium deposits (Burns 1999). Other important uranium ore minerals are: brannerite ($(U,Ca,Y,Ce)(Ti,Fe)_2O_6$); coffinite ($USiO_4 \cdot n\,H_2O$); and pitchblende (i.e. amorphous or poorly crystalline uranium oxide) (Finch and Murakami 1999). Uranium ore minerals commonly contain minor amounts of thorium, rare earth elements, lead, calcium, and other elements as cation substitutions (Lottermoser 1995). Uranium may also be present as minor substitution in rock-forming minerals or in accessory phases such as allanite, xenotime, monazite, zircon, apatite, and sphene. Uranium ore minerals weather easily, and numerous secondary uranium (U^{6+}) minerals are known from weathered uranium ores (Burns 1999). The gangue mineralogy of uranium ores is highly variable and deposit specific. Gangue minerals include framework, ortho, ring, chain and sheet silicates as well as sulfides, oxides, hydroxides, sulfates, phosphates, and carbonates.

Uranium ore grades are expressed in terms of triuranium octoxide (U_3O_8) which is 85% elemental uranium. Uranium ores exploited have ore grades as low as 0.01% to >0.5% U_3O_8. In addition, uranium ores have variably elevated metal and metalloid values (As, Cu, Mo, Ni, Pb, Ra, Re, Sc, Se, Th, V, Y, Zr) (e.g. Langmuir et al. 1999; Pichler et al. 2001). Arsenic, copper, lead, molybdenum, nickel, and selenium are commonly hosted by sulfide minerals. Sulfide minerals are ubiquituous in some uranium ores (e.g. roll front type uranium deposits). Uranium ores which contain abundant pyrite or marcasite may oxidize upon exposure, and AMD may develop in mine workings or mine wastes (Fernandes et al. 1998).

6.2.2
Placer and Beach Sands

Radioactive wastes not only accumulate as a result of uranium and phosphate mining but also during mining and processing of placer and beach sands. Placer and beach sands are sedimentary deposits which contain minerals with a high density, chemical resistance to weathering, and mechanical durability. Ore minerals include silicates, oxides, phosphates, and native elements (Table 6.1). The deposits are principally mined for their gold, diamond, sapphire, ruby, titanium (ilmenite, rutile), tin (cassiterite) or

Table 6.1. Examples of heavy minerals found in placer deposits and beach sands

Mineral name	Chemical formula
Cassiterite	SnO_2
Chromite	$FeCr_2O_4$
Columbite	$(Fe,Mn)Nb_2O_6$
Diamond	C
Gahnite	$ZnAl_2O_4$
Garnet group	$(Mg,Fe,Mn,Ca)_3(Al,Fe,Ti,Cr)_2Si_3O_{12}$
Gold	Au
Ilmenite	$FeTiO_3$
Magnetite	Fe_3O_4
Monazite	$(Ce,La)PO_4$
Platinum	Pt
Ruby	Al_2O_3
Rutile	TiO_2
Sapphire	Al_2O_3
Spinel	$MgAl_2O_4$
Tantalite	$(Fe,Mn)Ta_2O_6$
Xenotime	YPO_4
Zircon	$Zr(SiO_4)$

rare earth element (monazite, xenotime) contents. Some deposits may possess elevated uranium and thorium concentrations. In these deposits, the radioactive elements are present within chemically and physically stable, weathering resistant gangue minerals (e.g. monazite, xenotime, zircon, tantalite, columbite). The minerals effectively lock up the uranium and thorium in the crystal lattice and prevent mobilization of these elements and their radioactive decay products into the environment (Yusof et al. 2001). However, the minerals still emit radiation. Thus, exposure to radiation needs to be controlled, dust control measures need to be implemented, and appropriate handling methods of the radioactive wastes or ores need to be applied.

While the mining and mineral processing of alluvial tin deposits and heavy mineral sands do not result in the mobilization of radioactive elements into the environment, the metallurgical extraction of ore elements from such ores may. For example, the processing of titanium ores obtained from heavy mineral sands is based on sulfuric acid leaching. Acid leaching of titanium ores not only liberates titanium from the crystal lattices of rutile and ilmenite but also releases radionuclides and other metals from gangue phases. Consequently, spent process waters of titanium processing plants can exhibit very low pH values and high TDS concentrations (Schuiling and van Gaans 1997a,b).

6.3
Aqueous Chemistry of Uranium

Uranium is the typical constituent of surface and ground waters at uranium mine sites. It originates from the leaching of uranium ores as well as from the leaching of solid mining, processing and metallurgical wastes. An understanding of the leaching processes requires a knowledge of the aqueous chemistry of uranium. The aqueous behaviour of uranium can be described in terms of oxidative dissolution of uranium minerals, uranium solubility, and uranium precipitation.

6.3.1
Oxidative Dissolution of Uranium Minerals

The most reduced form of uranium (i.e. U^{4+}) is found in uraninite, coffinite, brannerite, and pitchblende. This oxidation state is the least soluble and least mobile form of uranium. In contrast, the most oxidized state of uranium (i.e. U^{6+}) is the most soluble and most mobile (Wanty et al. 1999). As a consequence, if oxygen is available as dissolved or gaseous species, U^{4+} can be oxidized to U^{6+}, and uranium dissolves in water as the uranyl oxyanion (UO_2^{2+}). The oxidative dissolution of uranium minerals is achieved progressively through a sequence of chemical reactions (Ragnarsdottir and Charlet 2000). A simplified overall reaction for the oxidative dissolution of uraninite is as follows:

$$2\,UO_{2(s)} + 4\,H^+_{(aq)} + O_{2(g)} \rightarrow 2\,UO^{2+}_{2\,(aq)} + 2\,H_2O_{(l)} \tag{6.1}$$

The oxidation of U^{4+} minerals (i.e. uraninite, coffinite, brannerite, pitchblende) can also be achieved by the oxidant Fe^{3+} (Abdelouas et al. 1999). The production of Fe^{3+} is possible through the indirect oxidation of iron sulfide minerals within the waste:

$$4\,FeS_{2(s)} + 14\,O_{2(g)} + 4\,H_2O_{(l)} \rightarrow 4\,Fe^{2+}_{(aq)} + 8\,H^+_{(aq)} + 8\,SO^{2-}_{4(aq)} + \text{energy} \tag{6.2}$$

$$4\,\mathrm{Fe}^{2+}_{(aq)} + 4\,\mathrm{H}^{+}_{(aq)} + \mathrm{O}_{2(g)} \rightarrow 4\,\mathrm{Fe}^{3+}_{(aq)} + 2\,\mathrm{H_2O}_{(l)} + \text{energy} \tag{6.3}$$

$$\mathrm{FeS}_{2(s)} + 14\,\mathrm{Fe}^{3+}_{(aq)} + 8\,\mathrm{H_2O}_{(l)} \rightarrow 15\,\mathrm{Fe}^{2+}_{(aq)} + 16\,\mathrm{H}^{+}_{(aq)} + 2\,\mathrm{SO}^{2-}_{4(aq)} + \text{energy} \tag{6.4}$$

In the initial step (Reaction 6.2), pyrite reacts with oxygen and water to produce dissolved Fe^{2+}, sulfate and hydrogen ions. The release of hydrogen with the sulfate anion results in an acidic solution unless other reactions occur to neutralize the hydrogen ions. The second step (Reaction 6.3) involves the oxidation of Fe^{2+} to Fe^{3+} and occurs at a low pH. The Fe^{3+} turn oxidizes pyrite via Reaction 6.4, which in turn produces more Fe^{2+}, and so on. The Reactions 6.2, 6.3 and 6.4 represent the indirect oxidation of pyrite (Sec. 2.3.1). However, the Fe^{3+} produced in Reaction 6.3 may not only oxidize reduced minerals such as pyrite but also reduced U^{4+} minerals like uraninite:

$$\mathrm{UO}_{2(s)} + 2\,\mathrm{Fe}^{3+}_{(aq)} \rightarrow \mathrm{UO}^{2+}_{2\,(aq)} + 2\,\mathrm{Fe}^{2+}_{(aq)} \tag{6.5}$$

The oxidation of uraninite (Reaction 6.5) generates dissolved uranyl oxyanions and Fe^{2+}. This Fe^{2+} can then be oxidized to Fe^{3+} via Reaction 6.3, which in turn oxidizes uraninite via Reaction 6.5, which in turn produces more Fe^{2+}, and so on. Reactions 6.3 and 6.5 form a continuing cycle of Fe^{2+} conversion to Fe^{3+} and subsequent oxidation of uraninite by Fe^{3+} to produce Fe^{2+} etc. This cycle continues until the supply of uraninite or Fe^{3+} to the reaction system is exhausted. While oxygen is not required for the Reaction 6.5 to occur, it is still needed to convert Fe^{2+} to Fe^{3+} (Reaction 6.3). Thus, pyrite oxidation produces acid and Fe^{3+}, and these two products enhance the leaching and destruction of uranium minerals. The resulting low pH conditions favour the dissolution of uranium, metals, and metalloids within solid uranium mine wastes.

Once uraninite, coffinite, brannerite, and pitchblende are exposed to atmospheric oxygen and water, they readily undergo oxidation and dissolution. Other reduced minerals such as sulfides in the wastes will also be oxidized. If the waste materials are depleted in acid neutralizing minerals, acid pore waters and leachates will develop. The AMD conditions favour the enhanced dissolution of uranium minerals and the transport of dissolved uranium as sulfate complexes. Consequently, the release of uranium, metals, and metalloids from solid uranium mine wastes is controlled by the availability of oxygen and water.

The oxidative dissolution of uranium minerals appears to be very similar to that of sulfides (Sec. 2.3): (*a*) there are certain bacteria which act as catalysts in the destruction of sulfides and uranium minerals (Ragnarsdottir and Charlet 2000); (*b*) the destruction of both mineral types can occur through biotic or abiotic and direct or indirect oxidation processes; (*c*) the destruction of the minerals is achieved progressively through a sequence of chemical reactions; and (*d*) various factors including solution pH, oxygen abundance, microbiological activity, and mineral surface area influence the rate of mineral dissolution.

6.3.2
Uranium Solubility

Uranium occurs in natural waters as U^{4+} and U^{6+} ions. The abundance of these uranium ions in water is influenced by the presence and abundance of complexing agents and the prevailing pH and Eh conditions.

Under reducing conditions and acid pH, uranium is present in water as the U^{4+} species. In the absence of ligands, the concentrations of dissolved U^{4+} never exceed µg l^{-1} levels (Ragnarsdottir and Charlet 2000). Under oxidizing conditions, conversion of U^{4+} to the higher state U^{6+} results in the formation of the highly soluble, stable and mobile uranyl ion (i.e. UO_2^{2+}). Solubility is enhanced by complexation with sulfate, carbonate, hydroxide, fluoride, chloride, nitrate, phosphate or organic ligands such as humic or fulvic acids (Langmuir 1997; Ragnarsdottir and Charlet 2000). Uranium is then transported as an anion or complexed anion in oxidized ground and surface waters. The concentrations of U^{6+} species in oxidized ground and surface waters reach tens or even thousands of mg l^{-1}, depending on pH and ligand concentrations (Ragnarsdottir and Charlet 2000). Alkaline pH values and elevated bicarbonate concentrations in oxidized ground and surface waters favour the stabilization and mobilization of uranium as uranyl carbonate complex (Abdelouas et al. 1998a). In contrast, the predominant species in acid, oxygenated waters are the uranyl ion and uranyl-sulfate complex (Wanty et al. 1999; Abdelouas et al. 1999). Thus, acid or alkaline oxygenated mine waters may carry significant concentrations of dissolved uranium.

Natural ground and surface waters contain several µg l^{-1} uranium, and much higher uranium concentrations are found in mineralized areas (Ragnarsdottir and Charlet 2000). At uranium mine sites, oxidative dissolution of uranium minerals can be extreme, causing strongly elevated uranium concentrations in mine waters. Leachates of uranium mine wastes may contain tens of mg l^{-1} uranium. The dissolved uranium can migrate many kilometers from its source until changes in solution chemistry lead to the precipitation of uranium minerals.

Leachates of uranium mine wastes may also have elevated thorium and radium-226 levels. Thorium is less soluble than uranium under all conditions. However, thorium may be mobilized in low pH mine waters (Langmuir 1997). Once in solution, the element readily coprecipitates with iron and manganese oxyhydroxides, or it precipitates if the pH increases to values above 5 (Wanty et al. 1999).

Thorium-230 is the long-lived parent (half-life: 80 000 years) of the radium isotope Ra-226. This radium isotope is commonly present in waters of uranium mines since it is soluble and mobile under acid conditions; yet high sulfate concentrations in acid mine waters limit the solubility of Ra-226. Sulfate minerals such as barite ($BaSO_4$), celestite ($SrSO_4$), anglesite ($PbSO_4$), gypsum ($CaSO_4 \cdot 2\,H_2O$), or jarosite may precipitate from the waters. These minerals incorporate radium in their crystal lattices, limiting Ra-226 mobility.

6.3.3
Uranium Precipitation

Precipitation of dissolved uranium is primarily achieved through the destruction of uranyl complexes. The stability of dissolved uranium is greatly influenced by: coprecipitation; adsorption onto clays or oxyhydroxides; decreasing Eh; microbiological activity; and composition of the solution. Hence, uranium can be removed from solution through the following processes (e.g. Erskine et al. 1997; Abdelouas et al. 1998a,b; Wanty et al. 1999; Ragnarsdottir and Charlet 2000):

- *Coprecipitation.* Coprecipitation of uranium with carbonates and iron or aluminium leads to the incorporation of uranium into carbonate minerals and iron or aluminium oxyhydroxides. The coprecipitation of uranium is reversible. For example, reduction and dissolution of solid uranium-rich iron oxyhydroxides release uranium back into the water column (cf. Sec. 3.5.9).

- *Adsorption.* Positively charged uranium may be adsorbed onto negatively charged surfaces of sulfides, clays and organic matter as well as iron, manganese and aluminium oxyhydroxide particles. Uranium adsorption is also reversible (cf. Sec. 3.5.4). Desorption of uranium back into solution may occur if the water chemistry allows redissolution of uranium (e.g. increasing abundance of carbonate complexes at an alkaline pH).
- *Decreasing Eh.* Uranium is a redox-sensitive element, and reaction of U^{4+}-bearing waters with organic matter or hydrogen sulfide leads to uranium precipitation. For example, reduction due to a reaction of uranyl complexes with organic matter (simplified as molecule CH_2O) results in the precipitation of U^{6+}. The precipitated uranium may form an insoluble uranium oxide (UO_2) or one of its hydrates (Reaction 6.6) that is stable under reducing conditions. Also, the reduction and precipitation of uranium can be due to reactions of uranyl complexes with hydrogen sulfide, which has been generated by bacteria living in an anaerobic environment (Reaction 6.7). Such reduction reactions can occur in stream sediments of humid temperate or tropical environments where organic material is abundantly available to accumulate uranium.

$$4\,UO^{2+}_{2\,(aq)} + CH_2O_{(s)} + H_2O_{(l)} \rightarrow 4\,UO_{2(s)} + CO_{2(aq)} + 4\,H^{+}_{(aq)} \qquad (6.6)$$

$$4\,UO^{2+}_{2\,(aq)} + HS^{-}_{(aq)} + 4\,H_2O_{(l)} \rightarrow 4\,UO_{2(s)} + SO^{2-}_{4(aq)} + 9\,H^{+}_{(aq)} \qquad (6.7)$$

- *Microbiological activity.* Microorganisms are capable of removing dissolved uranium from solution and incorporating it into their cell structure. Uranium may also be adsorpted onto the cell surface. In addition, microorganisms can directly convert dissolved U^{6+} to solid U^{4+} compounds. As a consequence, the amount of uranium dissolved in mine waters is reduced.
- *Decreasing pH and removal of the complexing agent from the water.* Uranium may precipitate with phosphate or carbonate ions to form secondary phosphate- or carbonate-uranium minerals. However, the precipitation of secondary uranium minerals is unlikely since mine waters are commonly undersaturated with respect to secondary uranium minerals (Wanty et al. 1999). Significant evaporation of waters has to occur to cause the formation of secondary uranium minerals.

6.4
Radioactivity

6.4.1
Principles of Radioactivity

An element is characterized by its defined number of protons whereas the number of neutrons for a particular element may vary, giving rise to several isotopes (Attendorn and Bowen 1997). For instance, uranium has 92 protons and either 146, 143 or 142 neutrons, giving rise to three different isotopes (i.e. U-238, U-235, U-234). Most lighter elements possess stable isotopes whereas the heavier elements tend to have unstable isotopes, which eventually disintegrate into new isotopes. These unstable or radioactive isotopes have an excess energy that is released during the decay in order to achieve a lower and more stable energy state. Unstable, radioactive atomic nuclei change their structure by absorbing or, more commonly, releasing protons, neutrons, electrons or electromagnetic waves to become nuclei of new isotopes. Such radioactive atomic nuclei are also referred to as "*radionuclides*" in order to stress the radioactive nature of these nuclides. Naturally occurring "*parent nuclides*" break up yielding "*daughter nuclides*". If the daughter nuclides are radioactive, they will decay further. Any radioactive decay will end with the formation of a stable isotope. The decay of radionuclides in a series of steps is a so-called "*decay series*". The various decay products of a decay series are referred to as "*progeny*". In this chapter, the term "radionuclides" is used to refer to the parent and daughter radionuclides of the uranium-238 (U-238), uranium-235 (U-235), and thorium-232 (Th-232) series.

The process of radioactive decay is associated with the release radiant energy (i.e. "*radiation*"), which takes the form of particles and electromagnetic waves. Radiation levels are assessed using the activity of the radioactive material. "*Radioactivity*" is defined as the number of disintegrations of an atomic nucleus per unit time. The decay of a radionuclide over time can be measured. The term "*half-life*" is used to describe the period of time during which half of the atoms of a particular radionuclide decay. Measured half-lifes vary from a fraction of a second to several thousand million years.

Radioactive nuclides differ from stable nuclei in that radioactive nuclides emit "*ionizing radiation*" in the form of: (*a*) alpha particles (i.e. a helium nucleus of atomic mass four consisting of two neutrons and two protons); (*b*) beta particles (i.e. highly energetic electrons); and (*c*) gamma-rays (i.e. high energy electromagnetic waves). Alpha particles do not penetrate matter deeply because of their large size and double positive charge. However, they cause an enormous amount of ionization along their short path of penetration. They travel only a few centimeters in air and can be stopped by a piece of paper or the outer layer of the skin. Hence, alpha particles present an insignificant hazard outside the body, yet they are a potential hazard when ingested or inhaled. Beta particles are more penetrating than alpha particles because of their smaller size and negative charge, but beta particles produce much less ionization than alpha particles. Beta particles travel a few meters in air and require a couple of centimeters of plastic to stop them. Gamma-rays have neither mass nor charge and are much more penetrating than particulate radiation. Gamma-rays have an infinite range in air and require several centimeters of lead to absorb them.

The three kinds of radiation have very different properties but all are energetic enough to break chemical bonds. The primary effects of alpha particles, beta particles, and gamma-rays are the removal of electrons from atoms and the production of ions in the materials they strike; therefore, the term "ionizing radiation" is used. Ionizing radiation has the potential to cause biological damage by two principal mechanisms. Firstly, the ionization radiation induces direct damage to atoms and molecules of living cells and tissue. Secondly, the ionization radiation causes indirect damage to water molecules in the organism, resulting in highly reactive free radicals and molecules (e.g. hydrogen peroxide) that are chemically toxic to the organism.

6.4.2
Radioactive Decay of Uranium and Thorium

Uranium is a naturally occurring radioactive element in the Earth's crust, and uranium ores are concentrations of such natural radioactivity. The radioactivity of uranium ores and wastes is caused by the decay of radioactive isotopes. Uranium has three natural isotopes: uranium-238 (U-238); uranium-235 (U-235); and uranium-234 (U-234); all of which are radioactive. The relative abundances of U-238, U-235, and U-234 are 99.28%, 0.71%, and 0.006%, respectively (Attendorn and Bowen 1997; Ragnarsdottir and Charlet 2000). These parent nuclides are unstable; they decay to daughter nuclides and release radiation in the form of alpha and beta particles as well as gamma-rays. In fact, U-238 and U-235 are the parent isotopes for various intermediate radionuclides, and U-234 is a decay product of U-238 (Ragnarsdottir and Charlet 2000). These intermediate nuclides decay further – via alpha or beta emission – to new nuclides which in turn decay to other radionuclides. Uranium-238 and U-235 are the head of two separate decay series, which ultimately yield the stable, non-radioactive daughter nuclides Pb-206 and Pb-207, respectively (Table 6.2). Uranium-235 is not as prevalent in nature as U-238 because of its shorter half-life and lower abundance than U-238. Consequently, radiation originating from the U-235 decay series is significantly less than that of the U-238 series.

Uranium occurs together with thorium in uranium ore deposits. Thorium has several isotopes including Th-234, Th-232, Th-231, Th-230, Th-228, and Th-227 (Attendorn and Bowen 1997). Thorium-232 is the most abundant radioactive isotope and head of the Th-232 series. It eventually decays via intermediate daughter isotopes to a stable lead isotope (Pb-208) (Table 6.2). Thus, the concentrations of uranium and thorium are naturally decreasing. The uranium and thorium isotopes have long half-lifes comparable to the age of our planet and hence, these isotopes are still present.

6.4.2.1
Radium

The radiogenic isotope radium-226 (Ra-226) is a daughter product of the U-238 series and a direct descendent of Th-230 (half-life: 80 000 years) (Table 6.2). While Th-230, Pb-210, and radon isotopes are of concern, Ra-226 is of most concern in uranium mining and processing operations because (Landa and Gray 1995; Kathren 1998; Landa 1999; Ewing 1999):

1. Radium-226 has a half-life of 1 622 years and therefore, persists in uranium mine wastes.
2. Radium-226 has similar geochemical and biogeochemical properties to its fellow group II elements (Ca, Ba, Sr) and forms compounds that can be taken up by humans, plants, and animals.
3. Radium-226 has a high radiotoxicity and affinity for accumulating in bones.
4. Compared to uranium and thorium, Ra-226 is readily liberated from the uranium ore minerals during natural weathering and mineral processing; it is more soluble than uranium and thorium; it may leach from soils, rocks, ores and mine wastes; and it is readily mobilized into ground and surface water.

Table 6.2. Simplified decay pathways and half-lifes of the U-238, U-235 and Th-232 series (after Brownlow 1996; Kathren 1998; Langmuir 1997)

Series	Isotope	Particle emitted	Half-life
U-238	U-238	α	4.5×10^{9} yr
	Th-234	β	24 d
	Pa-234	β	1.17 min
	U-234	α	247 500 yr
	Th-230	α	80 000 yr
	Ra-226	α	1 622 yr
	Rn-222	α	3.8 d
	Po-218	α	3 min
	Pb-214	β	26.8 min
	Bi-214	α, β	19.7 min
	Po-214	α	164 µs
	Tl-210	β	1.32 min
	Pb-210	β	22.5 yr
	Bi-210	β	19.7 min
	Po-210	α	140 d
	Pb-206	Stable	–
U-235	U-235	α	713×10^{6} yr
	Th-231	β	25.6 h
	Pa-231	α	34 300 yr
	Ac-227	β	22 yr
	Th-227	α	18.6 hr
	Ra-223	α	11.2 d
	Rn-219	α	3.9 s
	Po-215	α	1.83 µs
	Pb-211	α	36.1 min
	Bi-211	α, β	2.16 min
	Po-211	α	0.52 s
	Tl-207	β	4.79 min
	Pb-207	Stable	–
Th-232	Th-232	α	1.4×10^{10} yr
	Ra-228	β	6.7 yr
	Ac-228	β	6.13 hr
	Th-228	α	1.9 yr
	Ra-224	α	3.64 d
	Rn-220	α	54.5 s
	Po-216	α	0.15 s
	Pb-212	β	10.6 hr
	Bi-212	α, β	60.4 min
	Po-212	α	0.29 µs
	Tl-208	β	3.1 min
	Pb-208	Stable	–

5. Radium-226 decays by alpha emission to the important radon isotope radon-222 (Rn-222). Consequently, Ra-226 is the head and source of the important subseries that includes radon (Table 6.2).

6.4.2.2
Radon

Radon is a colourless, odourless and tasteless noble gas with three naturally occurring radioactive isotopes (i.e. Rn-219, Rn-220, Rn-222). The term “radon” commonly refers only to Rn-222 (Sharma 1997). Radon-219 is the daughter product of the U-235 series, Rn-220 is a member of the Th-232 series, and Rn-222 is a daughter product of the U-238 series and the direct descendent of Ra-226. The most abundant isotope is Rn-222 which is due to the abundance of its parent isotope U-238. The other two isotopes Rn-219 and Rn-220 are significantly less abundant, have shorter half-lifes, and are therefore of little environmental concern (Sharma 1997). In contrast, Rn-222 has a half-life of 3.8 days. Radon-222 is of concern in uranium mining and processing because:

1. Radon-222 is a descendant of parent radionuclides with long half-lifes (Th-230: half-life 80 000 years; Ra-226: half-life 1 622 years). As a result, Rn-222 represents a long-term hazard despite its short half-life of 3.8 days.
2. Radon-222 is a noble gas and soluble in water. Such properties allow radon to move freely in ground and surface waters.
3. Radon-222 itself decays by the emission of an alpha particle. The daughter products are polonium-218 (Po-218), lead-214 (Pb-214), and bismuth-214 (Bi-214), that is, the so-called "*radon progeny*". These solid daughter products are highly radioactive and emit alpha and beta particles as well as gamma-rays (Table 6.2).
4. Once Rn-222 is inhaled by humans, its radioactive solid decay products are deposited directly within the lungs. The lodged radon progeny will cause ionizing radiation and induce lung cancer.

In uranium mine environments, radon gas particularly emanates from uranium ores, mineralized waste rocks, and uranium mill tailings. Radon – released to pore spaces of mine wastes – migrates to the surface of the material or is dissolved in pore waters. Radon is also emitted from undergound workings and open pits. After the termination of mining, radon will continue to emanate from the walls and floor of mine workings. Since most of the ore is generally removed from mine workings, the primary sources of radon are the waste rock piles and any ore stockpiles. Local meteorological effects can control radon emanation from the ground, and radon emanation depends on air pressure, soil moisture, soil structure, ground cover, wind, and temperature (Nielson et al. 1991).

6.4.3
Units and Measurements of Radioactivity and Radiation Dose

6.4.3.1
Units

There is a confusing array of units to measure radioactivity. Fortunately, radiation units can be classified in two major categories (Nielson et al. 1991; Wilson 1994) (Table 6.3).

1. *Radioactivity.* The radioactivity of a material is measured by the number of nuclear disintegrations per unit of time. Thus, the units to describe radioactivity are based on nuclear disintegrations which are counted in units of time for a specific volume of radioactive material. The basic and fixed unit of radiation is the Curie (Ci) that is defined as the number of nuclear disintegrations per second. One Curie is equivalent to 3.7×10^{10} disintegrations per second which is the measured activity of 1 g ra-

Table 6.3. Radioactivity and radiation dose measurement units and their conversion (Nielson et al. 1991; Sharma 1997; Wilson 1994)

Unit	Definition	Conversion
Radioactivity = Nuclear disintegration per unit time per volume of radioactive material		
Bq (Becquerel)	One disintegration per second of a radioactive isotope	1 Bq = 27 pCi
Bq kg^{-1}	Specific activity of a radioactive isotope per unit mass	
Ci (Curie)	Activity of 1 g radium: 3.7×10^{10} disintegrations per second	1 Ci = 3.7×10^{10} Bq
Ci kg^{-1}	Specific activity of a radioactive isotope per unit mass	
pCi l^{-1}	Specific activity of a radioactive isotope measured in water	1 pCi l^{-1} = 37 Bq m^{-3}
R (Roentgen)	Radiation required to produce one electrostatic unit of charge in one cubic centimeter of dry air	1 R min^{-1} = 1 Ci
Radiation dose = Biological effects of nuclear disintegration		
Gy (Gray)	Absorbed radiation dose; corresponding to one joule of radiation absorbed per kilogram of tissue	1 Gy = 100 rad 1 Gy = 1 J kg^{-1}
Sv (Sievert)	Absorbed radiation dose measured in gray times the quality factor for the type of radiation and a weighting factor for the tissue irradiated; unit to describe the damage to tissue	1 Sv = 100 rem
REM	Roentgen equivalent in man; ionizing radiation equal to damage to humans of one roentgen of high voltage X-rays	1 rem = 0.01 Sv
rad	Radiation absorbed dose per unit mass	1 rad = 0.01 J kg^{-1}

dium. Radioactivity is also measured in Becquerel (Bq) which is defined as one disintegration per second of a radioactive isotope. The *specific radioactivity* of a nuclide in solid materials refers to the number of nuclear disintegrations per second per unit of mass (e.g. a tailings sample has 100 Bq kg^{-1} of Ra-226). In radon measurements, picoCuries per liter (pCi l^{-1}) are commonly used, and potable water standards and water analyses are given in this unit (e.g. a water sample has 10 pCi l^{-1} of Ra-226).

2. *Radiation dose.* The effects of radiation are assessed using the amount of radiation received by biological material. The amount of radiation received by a person is of prime interest in human health studies. The amount of radiation is measured by the "*radiation dose*" which refers to the amount of energy imparted per unit of biological mass. Rems, rads, Grays (Gy), and Sieverts (Sv) are all related to the radiation effects on humans. These units are not based on pure physical measurements but on radiation research, statistics, and multiplication factors. The term "rem" is often used to describe the dose that can be imposed upon humans. Rem is an acronym for "roent-

gens equivalent in man". Rad is the "radiation absorbed dose". Rem and rad relate to the Standard International (SI) radiation units Gray (Gy) and Sievert (Sv). The dose of energy that is absorbed in the body tissue is measured in Grays (Gy). Equal exposure to different types of radiation does not necessarily produce equal biological effects. One Gray of alpha radiation has a greater effect than one Gray of beta radiation. Radiation effects, regardless of the type of radiation, are measured in Sieverts (Sv). One Sievert of radiation deposits 0.01 J of energy per kilogram of tissue. Radiation exposure levels for the general public and maximum permissible radiation doses are given in milliSievert per year (mSv year^{-1}).

6.4.3.2
Measurements

Curies and Becquerels are laboratory measurements whereas counts per minute (cpm), milliSievert per hour (mSv hour^{-1}), and microRoentgens per hour (μR hour^{-1}) can be established in the field (Wilson 1994). Field gamma-ray spectrometers are used to measure the latter three units. Alpha and beta particles are best measured in counts per minute (cpm), using Geiger counters or scintillometers whereby the measured counts per second (cps) are roughly equivalent to disintegrations per second (Bq) (Wilson 1994). The levels of radionuclides found in water (U-238, U-234, Th-230, Th-232, Ra-226, Pb-210, Po-210) are typically measured in units of milliBecquerel per liter (mBq l^{-1}) or picoCuries per liter (pCi l^{-1}). The radionuclide of most concern in water is Ra-226.

The detection and measurement of radon is based on sniffer-type radon detectors. The soil gas or degassed water is thereby analyzed for its alpha activity since Rn-222 decays by alpha emission to Po-218 (Table 6.2). Alternatively, alpha-sensitive films buried in soil allow the determination of radon gas concentrations (Nielson et al. 1991; Sharma 1997). Details on field procedures and operational considerations of gamma-ray spectrometry and radon emanometry are given by Sharma (1997) and Nielson et al. (1991).

6.4.4
Radioactive Equilibrium and Disequilibrium

Uranium ores have a radioactive equilibrium or disequilibrium in the U-238, U-235, and Th-232 decay chains. In an equilibrium state, radioactive parent and daughter isotopes decay, and the decay products remain isolated with the parent radionuclide. An equilibrium is reached between the parent and daughter nuclides, and the specific activity (ie. the number of radioactive disintegrations per unit time per unit mass) of all decay products will be approximately equal. For example, an equilibrium is in place if the activity (pCi g^{-1}) in the U-238 decay chain will be the same for the parent nuclide U-238 and for the daughter nuclides (e.g. Th-230, Ra-226, Rn-222 and so forth). Disequilibrium is found in naturally disturbed deposits where mobilization of nuclides has occurred during or after radioactive decay, for instance, as a result of weathering. In such deposits, the specific activity of all decay products will be different. The difference is caused by the behaviour of individual nuclides according to their own chemistry and the preferential mobilization of individual nuclides. For example, the loss of parent nuclides from the ore reduces the activity of daughter nuclides which follow the parent in the decay series.

Mining and beneficiation do not significantly disrupt the radioactive equilibrium or disequilibrium of uranium ores whereas chemical processing does. Chemical processing of uranium ores aims to concentrate uranium and to reject all other elements, including the daughter nuclides of uranium isotopes (Table 6.2). The daughter nuclides become separated from the parent uranium nuclides and a radioactive equilibrium is no longer established. The concentrations of the daughter nuclides are no longer controlled by the parent nuclides. Uranium mill tailings are in pronounced radioactive *disequilibrium* since the parent nuclides (U-238, U-235) have been removed.

The disequilibrium of radionuclides in tailings materials or seepage precipitates can be used to evaluate radionuclide mobility in and from a tailings repository (e.g. Naamoun et al. 2000). Also, dissimilar specific activities of parent and daughter nuclides in waste rock dumps are an indication of the mobility of individual radionuclides. For example, if the waste material has Ra-226 activities (Bq kg^{-1}) different to those of the immediate parent isotope Th-230 (Bq kg^{-1}), the parent-daughter nuclide ratio (i.e. Th-230/Ra-226) is not unity, disequilibrium is present, and preferential leaching and mobilization of individual radionuclides have occurred.

6.5
Uranium Mining and Extraction

Traditionally, uranium is extracted from open pits and underground mines (Figs. 6.1, 6.2), and the mined ore is treated in hydrometallurgical plants on and near the mine site to yield uranium (i.e. hydrometallurgy). In addition to this conventional mining and extraction process, an alternative technique, the so-called "in situ leach" operation, is applied to some uranium ores.

6.5.1
Conventional Mining and Extraction

In conventional uranium mining and extraction, ores are obtained from underground or open pit mines. The ore is first crushed and/or powdered for uranium extraction and then leached. The process chemicals include acid (e.g. sulfuric acid, nitric acid) or alkaline solvents (e.g. sodium carbonate-bicarbonate, soda) as well as oxidants (e.g. sodium chlorate, ferric ion, hydrogen peroxide). Oxidizing conditions are essential to allow formation of the highly soluble U^{6+} complexes. The acid or alkaline leaching process is applied to heap leach piles, or more commonly, under controlled conditions in a hydrometallurgical plant. The acid or alkaline process of uranium extraction oxidizes the uranium (U^{4+}) present in the uranium minerals (e.g. uraninite) and dissolves the oxidized uranium (U^{6+}) as a sulfate or carbonate complex:

$$UO_{2(s)} + 4\,Na^{+}_{(aq)} + 2\,CO^{2-}_{3(aq)} \rightarrow UO_2(CO_3)^{2-}_{2(aq)} + 4\,Na^{+}_{(aq)} \qquad (6.8)$$

$$UO_{2(s)} + 2\,H^{+}_{(aq)} + SO^{2-}_{4(aq)} \rightarrow UO_2(SO_4)^{0}_{(aq)} + 2\,H^{+}_{(aq)} \qquad (6.9)$$

The process chemicals dissolve the uranium minerals, and an uranium enriched liquor is formed. This liquor is commonly referred to as "pregnant liquor". It contains apart from uranium a range of other elements such as rare earth elements which were

Fig. 6.1. Open pit of the Mary Kathleen uranium mine, Australia. Elevated gamma-ray readings in the open pit correspond to exposed ore lenses, the former haul road, and abandoned ore stockpiles (up to 16 mSv per year). Wallrock oxidation of reactive sulfides produces acidic solutions, yet buffering reactions prevent low pH conditions from developing. The open pit lake contains saline surface waters at a pH of 6.11 (salinity 0.15%; elevated Ca, SO_4, Cu, Fe, Mn, Ni, U and Zn values)

Fig. 6.2. Headframe of the Ronneburg underground uranium mine, Germany. Waste rock pile of uraniferous, carbonaceous shale is present behind the headframe

originally present as cation substitutions within the uranium minerals (Lottermoser 1995). After the solids have been removed by filtration or other methods, the solution is concentrated and purified using ion exchange or solvent extraction techniques. The impurities (e.g. metals, metalloids) are collected and disposed of with the tailings.

Ammonia is added to the liquor, and the uranium precipitates as yellow coloured ammonium diuranate which is referred to as "*yellowcake*". The yellowcake is then converted and refined to uranium trioxide concentrate (UO_3). Uranium in yellowcake is mostly U-238 (>99%), containing a small proportion of U-235 and trace amounts of other elements such as thorium and radium.

6.5.2
In Situ Leach (ISL) Operations

"*In situ leach mining*" (ISL) or "*solution mining*" leaves the buried ore in place. The technique extracts uranium by reversing the natural process which originally deposited the uranium. The uranium was naturally emplaced by uranium laden (U^{6+}), oxidized ground waters which moved through permeable aquifers. Once the uranium-rich waters encountered reducing conditions in the aquifers, the uranium precipitated to form reduced (U^{4+}) uranium ore minerals.

The ISL process uses an acid or alkaline leaching solution that is introduced to the ore by means of injection wells (OECD 1999) (Figs. 6.3, 6.4). The leaching solution consists of ground water and process chemicals. The solution attacks the (U^{4+}) uranium minerals and oxidizes the uranium which forms soluble uranium (U^{6+}) complexes. The uranium-bearing solution is then pumped to the surface through production wells, and the uranium is recovered from the solution. The barren solution is regenerated with process chemicals and circulated back into the aquifer for continued leaching.

An acid or an alkaline leaching process is used to extract uranium. In the acid ISL operation, the ground water will be reduced to a pH of approximately 2. The process uses sulfuric acid – in some cases hydrofluoric acid – and oxidants such as nitric acid, nitrate, hydrogen peroxide or dissolved oxygen (Reaction 6.9). The alkaline ISL scheme applies alkaline reagents including ammonia, ammonium bicarbonate, and sodium carbonate/bicarbonate (Reaction 6.8). The alkaline ISL scheme is considered to be more "environmentally acceptable" than acid ISL mining because ISL affected ground waters are technically easier to restore once mining ceases (OECD 1999). The addition of bacteria to the leaching solution has also been trialled. *Acidithiobacillus ferrooxidans* has been employed as a leaching agent to enhance the dissolution of uranium ore minerals and to extract uranium from low grade ores in Canada and the United States.

Fig. 6.3. Schematic cross-section of an ISL uranium mining operation. The ISL process uses an acid or alkaline leaching solution that is introduced to the ore by injection wells. The leaching solution dissolves uranium minerals; the uranium-bearing solution is then pumped to the surface through production wells; and finally, the uranium is recovered from the solution in the processing plant

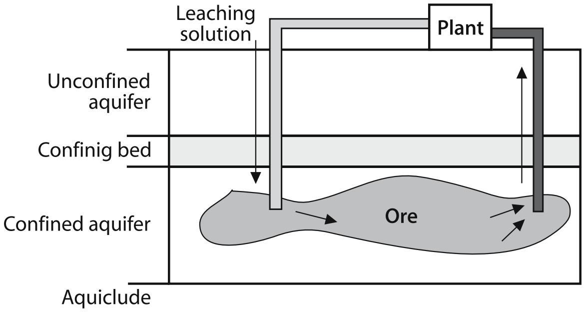

Fig. 6.4. Borefield of the Honeymoon ISL uranium mine, Australia. An acid leaching process is applied to a confined aquifer

The ISL mining technique is well established and has been used in various countries including former East Germany, Bulgaria, Ukraine, China, Kazakhstan, Uzbekistan, Czech Republic, the United States, and Australia (Mudd 2001a,b). Uranium deposits suitable for ISL mining occur in near surface permeable sand or sandstones, are located below the ground water table, and are confined by impermeable strata in the foot and hanging walls (Fig. 6.3).

Proponents of the ISL technique argue that the ISL method is applied to an unusable ground water resource and that it is controllable, safe, and environmentally benign compared to conventional open pit or underground mining techniques (Uranium Information Centre 2001a). In many cases, mining is conducted on a confined aquifer. The aquifer is naturally saline and contains naturally elevated levels of radionuclides and sulfate, which are present at concentrations well in excess of those considered safe for stock or domestic use. Furthermore, an ISL mining operation does not produce tailings, ore stockpiles, and waste rock dumps. Surface disturbances are minimized and environmental impacts are much less than for conventional mining. Finally, most of the radionuclides remain in the ore horizon, and there is a minimal increase in radon release and dust contamination from mined and processed ore. Mine waters contain radionuclides, and small quantities of radioactive sludges accumulate at ISL processing plants. The sludges need to be disposed of in lined waste repositories. The mine waters are either reinjected back into the aquifer, or they are applied as irrigation waters to designated land.

Opponents of the ISL technique argue that it is not an acceptable mining method. The acid ISL scheme requires monitoring and controlling of ground water conditions to ensure isolation of the affected aquifer from other ground water resources. Post-mining concentrations of some constituents (U, Ra-226) have been found to be elevated in the ground water when compared to pre-mining conditions (Caldwell and Johnson

1997). Once mining ceases, ground water restoration of the leached aquifer to pre-mining conditions is difficult if not impossible to achieve. Over time, mobilized and precipitated mineral particles such as clays, gypsum or jarosite will become trapped in the pore spaces (Mudd 2001a). The permeability of the leached ore horizon will be reduced, and the hydrology of the horizon is irreversibly changed. Acid ISL mining was not successful in the United States because of high acid consumption in carbonate-bearing aquifers and problems with ground water restoration after acid leaching (Mudd 2001a). In contrast, acid ISL operations were common in Eastern Europe and the former Soviet Union (Mudd 2001a). Where used in inappropriate locations, acid ISL mining resulted in significant ground water contamination in Bulgaria, the Czech Republic, and East Germany (Case Study 6.1).

Ground water restoration programs at former ISL sites rely on various techniques (e.g. reverse osmosis, volume reduction by evaporation, pump-and-treat). Contaminants are extracted from the ground waters, and some components may even be recycled including sulfuric acid, aluminium oxide, ammonia, and gypsum. Moreover, natural attenuation processes within aquifers can restore contaminated ground waters in ISL environments. The key geochemical processes which naturally remove dissolved radionuclides and heavy metals from ground waters are: (*a*) anaerobic conditions resulting in precipitation of reduced compounds such as uranium minerals and sulfides; (*b*) coprecipitation of uranium with iron oxyhydroxides, organic matter, and carbonates; and (*c*) adsorption of uranium on clay minerals, silicates, and aluminosilicates (Erskine et al. 1997). Such natural restoration mechanisms will of course only operate if the aquifer is anaerobic or contains elevated organic carbon, sulfide, clay as well as iron and manganese oxyhydroxide concentrations.

6.6

Mining, Processing and Hydrometallurgical Wastes

Wastes of uranium mining, processing and hydrometallurgical extraction are invariably radioactive. Most uranium mine wastes can be classified as non-radioactive (e.g. overburden, waste rocks) or low-level radioactive wastes (e.g. mine water, heap leach piles, waste rocks, tailings). Low-level radioactive wastes contain low levels of nuclides, emitting alpha and beta particles and gamma-rays. The greatest volume of non-radioactive and low-level radioactive waste products is generated at uranium mines that use conventional mining and extraction methods. At these locations, mining, processing and hydrometallurgical uranium recovery generate mine waters, sludges, waste rock dumps, heap leach piles, and tailings. In comparison, uranium mines using ISL techniques produce significant less waste and generate smaller volumes of radioactive mine waters and sludges. Wastes of uranium mining and extraction can be grouped into the following four categories:

- *Tailings.* Uranium extraction at many operating uranium mines is based on: (*a*) crushing of the ore to a fine powder; and (*b*) leaching the powdered ore with process chemicals in a hydrometallurgical plant. The solids are removed from the process circuit and pumped with spent process waters to a tailings repository. These wastes are referred to as "*uranium tailings*" or more commonly as "*uranium mill tailings*".

Case Study 6.1. Waste Production and Environmental Impacts of the Wismut Uranium Mines, Germany

Mining

During the Cold War, much of the Soviet Union's uranium for nuclear energy and weapons was obtained from mines in former East Germany. The operation was known as "Wismut" and subject of utmost secrecy (Mager and Vels 1992). The mining activities were extraordinary large. Underground workings include 280 mine shafts and several thousand kilometers of drifts, ramps, and drives. Between 1946 and 1990, 220 000 t of uranium were produced. The uranium production – in terms of historical uranium production from 1946 to 1989 – was the third largest in the world after the United States (330 000 t) and Canada (230 000 t). The production exceeded that of Australia (45 000 t), South Africa (138 000 t), and even the Soviet Union (190 000 t). However, the production costs of Wismut's uranium were probably ten times the actual market value of uranium. Resource extraction was among the world's most inefficient (Mager and Vels 1992).

Environmental Impacts and Rehabilitation

From 1946 to 1953, mining was practically carried out without considering damage to the environment or effects on humans. During that time, almost no radiation protection existed for the German miners. Mean annual radiation exposures were at 40 times higher than current radiation protection standards, and thousands of miners suffered from lung and liver cancer as well as leukaemia. There was no restoration concept or funds set aside for rehabilitation. Only minor rehabilitation work was carried out during exploitation. Mining continued from 1954 to 1990 and ceased with the reunification of Germany in 1990. Following mine closure, the total area of mining and milling sites held by Wismut was 37 km^2, and the total area affected by mining was 240 km^2. In 1991, the Soviet Union was released from its obligations for the decommissioning and rehabilitation, and ownership was transferred to the German government. The German government initiated a gigantic program to clean-up the former underground and open pit mines, mill sites, dump sites, buildings, ore stockpiles, soils, river beds, tailings ponds, and contaminated aquifers. The former uranium mining and processing sites were scattered over an area of 100 km by 60 km, and a total of 120 km^2 were assessed for the environmental database. A total surface area of 37 km^2 had to be remediated, including 22.5 km^2 of mine waste rock dumps and tailings. The environmental problems were serious because of the high population density in the region.

Waste Production

A total volume of 240 Mt of ore and 760 Mt of waste rock were produced from numerous underground and open pit mines. Open pit mining produced 600 million m^3 of ore and waste rock (Mager and Vels 1992; OECD 1999; Mudd 2001b). Most of this material has been backfilled into open pits. Rehabilitation efforts also focus on the stabilization, reshaping, cover, and revegetation of waste rock piles. The waste materials contain considerable amounts of pyrite, resulting in significant acid generating potential. In total, there were 70 waste dumps with a combined volume of 317 million m^3, covering an area of about 15 km^2. Mineral processing activities used numerous milling plants, ponds, sedimentation plants, and tailings dams. Tailings were produced using alkaline and acid leaching techniques, and the tailings were disposed of in very large ponds. At Crossen, the pond was 2 km^2 in size and contained approximately 45 million m^3 of tailings and 6 million m^3 of water. At Seelingstädt, the tailings were disposed of in two ponds, covering 3.4 km^2 with a volume of 107 million m^3. Some of the tailings dams were constructed on geological faults and are located in an seismically active region. The repositories require careful rehabilitation considering seismic stability, liquid and solid contamination potential, and radiation exposure.

- *Mine water.* Water contaminated with radionuclides, heavy metals, metalloids, and other constituents is commonly generated at an uranium mine site. Such water includes: mill water; process water; mining water from the dewatering of underground

Case Study 6.1. ***Continued***

ISL Operations

The Wismut operation also used in situ leach (ISL) techniques to recover uranium from subsurface ores (Mager and Vels 1992; OECD 1999; Mudd 2001b). At Königstein, mining activities and ISL operations severly disturbed a layered ground water system. Dilute sulfuric acid was injected into the orebody after blasting. The acid dissolved the uranium minerals, and the uranium-bearing solutions were pumped to the surface for processing and uranium recovery. This extraction technique left 2 million m^3 of dilute sulfuric acid with dissolved heavy metals in local aquifers. The leaching process chemically affected more than 55 million m^3 of rock and aquifer. Approximately 2 650 million liters of mine water – containing sulfuric acid and uranium – circulated or were trapped in the pore space of the rocks. The trapped waters have arsenic, cadmium, nickel and uranium levels up one to three orders of magnitude higher than German water quality guidelines. While the mine was in operation, there was little ground water contamination because the water flowing into the mine was pumped away from the acidified orebody. However, with the cessation of mining, pumping of working areas ceased, and the ground water may become contaminated because of the mixing of inflowing ground water with the remaining acid. Ground water restoration is essential because one aquifer of the layered ground water system is used by residents of the region for their water supply.

Conclusions

Intense uranium mining was conducted by the Soviet Union in former occupied East Germany over 45 years. The mining activities left a massive environmental disaster in a densely populated area. Like all centrally planned economies, at the time of mine closure there were no financial reserves to fund these activities. The total cost for decommissioning and rehabilitation has been estimated at 7 000 million EURO, and this will take at least until 2007 to complete.

and open pit mines; and seepage water emanating from waste rock dumps, heap leach piles and ore stockpiles. Contaminated water is also produced in association with ISL operations and during ground water restoration of former ISL activities. Contaminated waters require treatment prior to disposal or even discharge of the mine lease.

- *Waste rocks.* Country rocks enclosing uranium ores possess no or subeconomic amounts of uranium minerals, and the mined waste rocks display variable uranium concentrations as well as radioactivity and radon levels.
- *Heap leach residues.* At some mine sites, uranium is removed from low-grade ore using heap leaching. The leaching solution is sprayed on top of the pile. The solution percolates downwards until it reaches a liner below the pile where it is caught and pumped to a processing plant. Together with waste rock piles, heap leach piles represent a potential hazard during operation because of the possible release of dust, radon, and seepage waters. If waste rock dumps or heap leach piles are sulfidic, there may be a potential for AMD development in the long term.

6.7
Tailings

Uranium mill tailings are generally disposed of as a slurry. The tailings are best described in terms of solids and liquids. The solids can be further subdivided based on their particle size into slimes and sands. Each of these three tailings components (i.e. sands, slimes, tailings liquids) have distinct chemical, mineralogical and radiochemical properties (Table 6.4).

Following placement into a tailings repository, the slimes and sands will settle, and the tailings liquids can be decanted for reuse in the uranium extraction circuit. The pH of sulfuric acid tailings is generally less than 4 whereas the pH of the alkaline tailings is generally greater than 9 (Table 6.4). In both leaching processes, most of the uranium minerals are dissolved, and the gangue minerals present in the ore are attacked by the solutions. This creates tailings with high concentrations of dissolved and soluble salts, metals and radionuclides.

6.7.1
Tailings Radioactivity

The hydrometallurgical processing of powdered uranium ore is very selective for uranium and removes most of the uranium from the ore. The extracted uranium is only weakly radioactive because of the long half-life of U-238, and the uranium oxide concentrate contains approximately 15% of the initial radioactivity of the uranium ore (OECD 1999).

Table 6.4. The components of uranium mill tailings and their characteristics (US DEO 1999)

Tailings component	Particle size (µm)	Chemical composition	Mineralogical composition	Uranium content and radioactivity
Sands	>75	Major SiO_2 with <1 wt.% Al, Fe, Mg, Ca, Na, K, Se, Mn, Ni, Mo, Zn, V, U	Mostly gangue minerals of the original ore	0.004–0.01 wt.% U_3O_8 *Acid leaching:*[a,b] 26–100 pCi Ra-226 g^{-1}; 70–600 pCi Th-230 g^{-1}
Slimes	<75	Major SiO_2 with <1 wt.% Al, Fe, Mg, Ca, Na, K, Se, Mn, Ni, Mo, Zn, V, U	Mostly fine-grained gangue minerals of the original ore and clay minerals, oxides, fluorides, sulfates and amorphous substances	U_3O_8 and Ra-226 concentrations are almost twice the concentrations present in the sands *Acid leaching:*[b] 150–400 pCi Ra-226 g^{-1}; 70–600 pCi Th-230 g^{-1}
Liquids	–	*Acid leaching:* pH 1.2–2.0; Na^+, NH_4^+, SO_4^{2-}, Cl^-, and PO_4^{3-}; total dissolved solids up to 1 wt.%	–	*Acid leaching:* 0.001–0.01% U; 20–7 500 pCi Ra-226 l^{-1}; 2 000–22 000 pCi Th-230 l^{-1}
		Alkaline leaching: pH 10–10.5; CO_3^{2-} and HCO_3^-; total dissolved solids up to 10 wt.%	–	*Alkaline leaching:* 200 pCi Ra-226 l^{-1}; essentially no Th-230 (insoluble)

[a] U_3O_8 content is higher for acid leaching than for alkaline leaching.

[b] Separate analyses of sands and slimes from the alkaline leaching process are not available. However, total Ra-226 and Th-230 contents of up to 600 pCi g^{-1} of each isotope have been reported for the combined sands and slimes.

Hydrometallurgical processing does not achieve complete extraction of uranium from the ores, and discarded tailings always contain small amounts of uranium. Moreover, most of the undesired daughter radionuclides of the U-238 and U-235 series end up in the tailings, and the tailings carry the remaining 85% of the initial radioactivity of the uranium ore (Landa 1999; OECD 1999; Abdelouas et al. 1999). As a consequence, uranium mill tailings constitute a high volume, low-level radioactive waste. The radioactivity is caused by: (*a*) highly radioactive nuclides with relatively short half-lifes (e.g. Po-218, Po-214, Po-210, Pb-210); and (*b*) less radioactive nuclides with long half-lifes (e.g. Th-230, Ra-226) (Table 6.2). If the uranium ore is enriched in thorium, the tailings will possess abundant daughter nuclides of the Th-232 series. Hence, radiation levels and radon emissions from tailings are potentially significant, and the radioactivity of uranium tailings is greater than that of the yellowcake or uranium oxide concentrate.

6.7.2
Tailings Solids

In general, tailings solids can be: (*a*) primary ore and gangue minerals; (*b*) secondary minerals formed during weathering; (*c*) chemical precipitates formed during and after mineral processing; and (*d*) chemical precipitates formed after disposal in the tailings storage facility (Sec. 4.2.3). In the case of uranium mill tailings, the chemical precipitates form: (*a*) during and after hydrometallurgical extraction; (*b*) upon neutralization of acid tailings with lime prior to their disposal; and (*c*) after disposal of the tailings in the storage facility.

The tailings solids can be crystalline, poorly crystalline, and/or amorphous in nature, and they contain radionuclides, heavy metals, and metalloids (e.g. Langmuir et al. 1999; Pichler et al. 2001). The solids are insoluble or potentially soluble (Willett et al. 1994; Landa 1999; Donahue et al. 2000). Detailed analyses have revealed that radionuclides (i.e. Th-230, Ra-226, U-235, U-238), heavy metals, and metalloids are present in: (*a*) ion exchangeable, carbonate and readily acid soluble forms; (*b*) iron and manganese hydrous oxides; (*c*) fluorides; (*d*) alkaline earth sulfates (e.g. $BaSO_4$, $SrSO_4$); (*e*) organic matter; (*f*) sulfides; and (*g*) arsenates (Willett et al. 1994; Landa and Gray 1995; Somot et al. 2000; Donahue et al. 2000; Pichler et al. 2001; Donahue and Hendry 2003; Martin et al. 2003). The stability of these solid phases determines the potential mobilization of radionuclides, heavy metals, and metalloids into tailings pore waters.

Radium-226 is a radionuclide of significant concern in uranium mining. It tends to be concentrated in the fine fraction of uranium tailings (Landa and Gray 1995) (Table 6.4). Barium and radium have similar geochemical properties, including the low solubility of their sulfate salts and the coprecipitation of radium with barium as solid sulfates ($Ba(Ra)SO_4$). In addition, adsorption and coprecipitation processes lead to the fixation of Ra-226 in iron oxyhydroxides, feldspars, clays, amorphous silica, organic matter, sulfides, barite, and other sulfate grains. Iron oxyhydroxides and alkaline earth and lead sulfates play an important role in the fixation of Ra-226 and other radionuclides in acid tailings materials (Landa and Gray 1995; Goulden et al. 1998; Landa 1999; Somot et al. 2000; Martin et al. 2003).

Uranium tailings like all tailings undergo chemical reactions in a tailings repository (cf. Sec. 4.2.3). Over time, the tailings mineralogy and pore water composition may change. Dissolved radionuclides, metals, and metalloids may: (*a*) persist in solution;

(*b*) precipitate or coprecipitate by interacting with other components in the tailings; or (*c*) be adsorbed by tailings solids such as quartz, kaolinite, clays or amorphous substances (Landa and Gray 1995; Landa 1999). The potential release of radionuclides, metals and metalloids from tailings solids into pore waters and the presence of these elements in solution are undesirable. Tailings liquids laden with contaminants can escape from the tailings storage area and may impact on aquifers or surface waters. Consequently, the mineralogical siting and chemical reactions in uranium tailings need to be understood in order to determine the long-term behaviour of radionuclides, metals and metalloids in the waste repositories. The mobilization of radionuclides, heavy metals, and metalloids from tailings solids into tailings liquids can be induced through various factors (Landa and Gray 1995):

- *AMD development.* Tailings may contain abundant sulfide minerals that can oxidize in the tailings impoundment. The acid producing reactions may not be sufficiently buffered by acid neutralizing reactions, and this leads to the formation of AMD. The development of AMD in uranium tailings, heap leach piles and waste rock dumps will enhance the dissolution of uranium minerals and the mobility of radionuclides.
- *Presence of process chemicals.* Hydrometallurgical extraction schemes add significant amounts of sulfuric acid, alkaline materials, nitrate, chloride and/or organic solvents to the processed ore. The process reagents can leach host phases and act as complexing agents for radionuclides and heavy metals. The contaminants may be mobilized from their host minerals and dissolved in tailings waters.
- *Acid leaching or reduction of iron and manganese oxyhydroxides.* Iron and manganese oxyhydroxides represent important host phases to radionuclides, metals, and metalloids, in particular arsenic. These hosts can become unstable under acid or reducing conditions (e.g. Pichler et al. 2001). The establishment of acid or reducing conditions in uranium tailings may lead to dissolution of oxyhydroxides and to the mobilization of the previously fixed radionuclides, metals, and metalloids.
- *Bacterial reduction.* Sulfate and iron reducing bacteria within tailings can favour enhanced dissolved Ra-226 concentrations. The bacteria reduce solid sulfates and iron oxyhydroxides to sulfides and allow the release of radium from sulfate salts (Martin et al. 2003). The bacteria also convert dissolved sulfate to sulfide and keep the dissolved sulfate concentrations at relatively low levels. Low sulfate levels prevent the formation of insoluble sulfates and the fixation of Ra-226 as $Ba(Ra)SO_4$. The undesired release of Ra-226 into solution can occur through engineering measures or natural processes that cause low dissolved oxygen concentrations in tailings liquids.
- *Presence of clay minerals.* Clay minerals act as sinks for barium and strontium cations in tailings dams. The cations are incorporated into the clay structure which prevents the formation of insoluble alkaline earth sulfates and the coprecipitation of Ra-226 as $Ba(Ra)SO_4$. Abundant clay minerals within tailings may greatly enhance the concentration of Ra-226 in solution.

6.7.3
Tailings Liquids

Tailings liquids represent the surface and pore waters of tailings storage facilities. The tailings liquids tend to contain high concentrations of radionuclides, heavy metals, and metalloids. If neutralization has not been applied to the liquids of an acid leach plant, the tailings liquids are typically acid, saline and enriched in heavy metals, metalloids, radionuclides, iron, manganese, aluminium, alkalis (Na, K, Ca, Mg), sulfate, chloride, fluorine, and process chemicals (Landa 1999). Acid tailings liquids are commonly in equilibrium with a range of secondary salts such as gypsum and aluminium sulfates, which invariably precipitate and redissolve in the waste repository.

At some mine sites, tailings of an acid leach uranium processing plant are partly or completely neutralized with lime prior to discharge to a tailings storage facility. The tailings become saturated with calcium sulfate. The neutralization may result in the precipitation of gypsum and of numerous elements that were in solution in the acid process water (e.g. Fe, Cu, Mn, Mg). The chemical precipitates are primarily metal hydroxides and gypsum.

In the waste repository, natural neutralization of acid tailings liquids may occur through the reaction of tailings liquids with tailings solids. Dissolution of carbonate minerals or amorphous solids and the ion exchange uptake of hydrogen by clay minerals represent possible buffering reactions (Landa 1999). If the acidic tailings liquids react with aluminosilicate minerals, then secondary clay minerals, jarosite, and alunite will be produced. These minerals will plug pore spaces and decrease tailings permeability (Sec. 2.6.4). The minerals will also act as adsorptive sinks for radionuclides and heavy metals (Landa 1999). Such neutralization reactions promote the fixation of radionuclides and metals in tailings solids and reduce the ingress of oxygen and water into the waste. On the other hand, acidic tailings solutions may react with a clay liner placed at the bottom of tailings storage facility. A breach of the clay liner may then be possible.

6.7.4
Tailings Disposal

The specific radioactivity of uranium mill tailings is low (a few Ci kg^{-1}) relative to most other radioactive wastes produced during atomic weapon and nuclear power production. However, large quantities of uranium mill tailings have accumulated and today, there are probably more than 500 Mt of uranium tailings located around the world (Waggitt 1994). Long-term containment of these low-level radioactive wastes is of great environmental concern. Radionuclides can be leached out of these wastes which may result in the contamination of surrounding ground and surface waters, soils, and sediments. Current disposal practices aim: (*a*) to isolate tailings for a long period of time from the surrounding environment; (*b*) to prevent leakage from the repository; and (*c*) to protect ground and surface waters from contamination. The disposal of long-term radioactive, fine-grained, sulfidic or even acidic mine wastes requires special attention.

In the past, uranium mill tailings were often abandoned and left unrehabilitated, or they were discharged into local creek and lake systems. Today, finite disposal options for uranium tailings include: (*a*) placing them under water in a lake, ocean or wetland environment (e.g. MEND 1993b); (*b*) backfilling them into a mined-out open pit (cf. Sec. 4.5); and (*c*) dumping them into a tailings dam. The disposal of uranium mill tailings into open pits and tailings dams are the main waste management strategies:

- *Backfilling.* In-pit disposal of radioactive wastes has numerous advantages compared to conventional tailings dam disposal including: (*a*) the tailings are as secure physically as the original ore; (*b*) there is no hydraulic head due to the position of the tailings below ground, and there is less prospect of contaminants being leached; and (*c*) a greater depth of cover is achieved ensuring radiation safety. Uranium tailings like all other tailings are not simply very fine-grained ore particles (Sec. 4.2.3). Tailings undergo diagenesis, and their mineralogy and chemistry are unlike those of the originally mined ore. In particular, tailings contain soluble salts. These chemical precipitates may dissolve once the tailings become part of the local aquifer. Moreover, the tailings contain interstitial pore waters with reactive process chemicals and dissolved metals, metalloids, and radionuclides. If the open pit is not lined with clay or other impermeable liners, tailings solids and liquids will become part of the local aquifer, and water-rock reactions may lead to the mobilization of contaminants into ground waters. Alternatively, a highly permeable layer is installed around backfilled tailings to allow free ground water circulation (Fig. 6.5). Since the permeability of the tailings is lower than that of the permeable layer, it is likely that there will be no exchange of contaminants between tailings and ground water.
- *Tailings dams.* The disposal of uranium mill tailings into tailings dams has been and will continue to be the main waste management strategy. Deposition of tailings on engineered impermeable clay layers or geotextile liners can limit the seepage into underlying aquifers. However, at many inactive tailings dam sites liners have not been used, and migration of contaminants into the ground water has occurred. Once mining ceases, uranium tailings dams require permanent dry or wet covers, and conventional dry cover designs for uranium tailings are multi-layer barriers. Dry covers are best achieved using a combination of materials including geotextile liners. Tailings are covered with compacted and/or uncompacted waste rock or clay to minimize water ingress and to reduce gamma radiation and radon emanation levels (Fig. 6.6). An impermeable cap of clay and geotextiles can inhibit rainwater inflow and radon escape. Crushed waste rock above the clay will facilitate drainage from

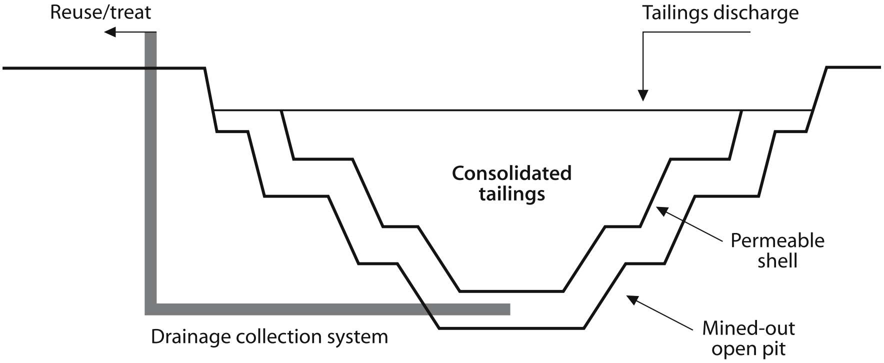

Fig. 6.5. Schematic diagram showing the in-pit disposal concept of uranium mill tailings (after Ripley et al. 1999). Consolidated tailings are discharged into a mined-out open pit that is lined with permeable, benign waste materials. Seepage waters are collected and treated or returned to the processing plant

the waste repository and reduces capillary suction forces. Topping with a suitable substrate, creating a gentle slope, and revegetation using local native species complete the rehabilitation of dry capped tailings dams (Fig. 6.7). The growth of vegetation with long roots should be avoided as this may lead to the disturbance of an intact cover and associated radon escape and radionuclide migration. The placement of a rock cover (so-called "riprap") has been used on tailings repositories in arid regions where rainfall is too low to support vegetation (Rager et al. 1996).

6.7.5
Long-term Stability of Tailings Dams

The design of an uranium tailings dam is important as the repository has to isolate the radionuclides and other contaminants and prevent them from entering the environment. Tailings dams or waste rock dumps are commonly rehabilitated using dry covers. The covers are designed: (*a*) to contain the waste; (*b*) to shed water; (*c*) to convert waste materials into landforms which comply with the final land use; and (*d*) to remain exceptionally stable over a significant period of time.

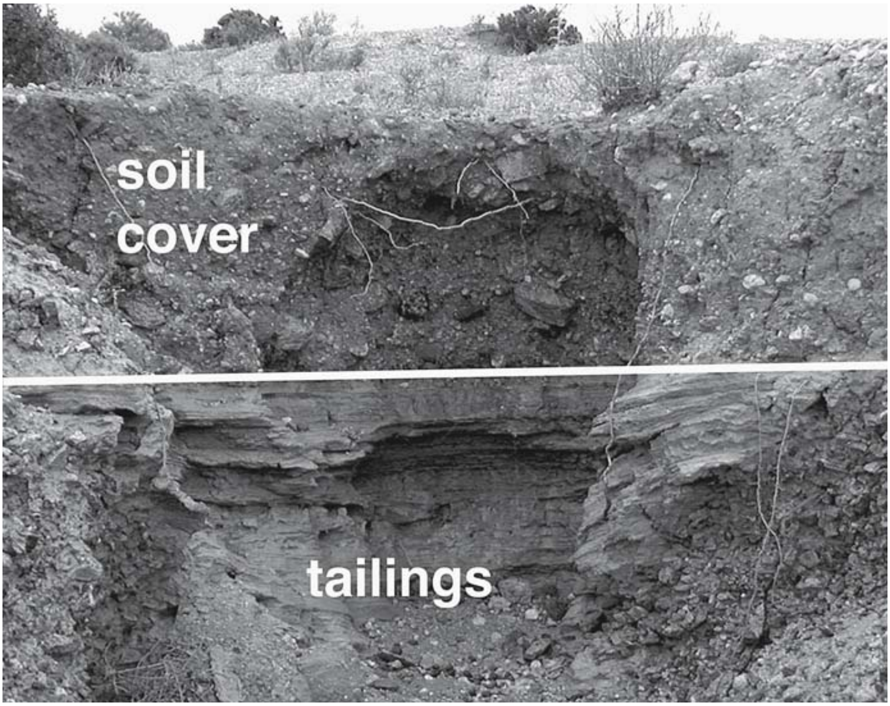

Fig. 6.6. Erosion and incision into a covered uranium mill tailings repository, Radium Hill, Australia. The tailings (30.6 mSv per year) were originally placed into a depression of crushed waste rock and then capped with soil containing calcrete and rock fragments. The soil cover reduces the radiation levels to 0.91 mSv per year as measured at the cover's surface

Fig. 6.7. Rehabilitated tailings dam at the Mary Kathleen uranium mine, Australia. The tailings dam has been rehabilitated using a multi-barrier system (clay and waste rock layers, vegetation cover). Piezometers allow sampling and monitoring of tailings liquids

The design features of uranium tailings dams are no different to those of other tailings dams. In Australia and the United States, above ground structures for the containment of tailings are required to have an engineered design life of at least 200 years and an effective structural life of up to 1 000 years (e.g. Code of Practice on the Management of Radioactive Wastes from the Mining and Milling of Radioactive Ores). However, uranium tailings contain radioactive isotopes with half-lifes (Th-230: 80 000 years; Ra-226: 1 622 years) that exceed the engineered design and structural life of tailings dams.

The long-term performance of dry covers is dependent on their resistance to wind and water erosion. In regions with high erosion rates (e.g. tropical regions with high intensity rainfalls), the long-term stability of capped uranium tailings dams is particularly important. The slope, thickness and permeability of cover materials and their resistance to erosion become crucial design features of tailings dams and waste rock dumps. Mine waste repositories are commonly designed as raised repositories and represent topographic highs in the surrounding landscape. These artificial landforms are subject to natural erosion once rehabilitation of the repositories has ceased. Erosion will eventually result in the leveling of any topographic expressions. If significantly elevated dumps are constructed in regions with high erosion rates, it has to be established whether the covers will protect the waste repositories from erosion in the long term.

Modeling, based on the universal soil loss equation or other techniques, can indicate whether a cover design or a post-mining landscape will remain viable at a mine site for an adequate number of years (East et al. 1994; Hancock et al. 2006). In addition, erosion studies for surrounding landforms can be used to estimate for how long wastes will be contained in waste repositories. Such modeling attempts are particularly important for the construction and evaluation of uranium tailings dams which are designed to isolate radioactive isotopes from the environment. The relative magnitude of the radioactivity and the long half-lifes of particular radionuclides in uranium tailings present a problem for the very long term (i.e. >1 000 years) (Landa and Gray 1995). Uranium tailings dams have to be secure and stable for over a period of several tens of thousands of years, so the long-term containment of uranium tailings in engineered structures is an important aspect of uranium mine waste management.

Despite their general acceptance and widespread use in the mining industry, the long-term stability and performance of capped repositories are unknown. While modeling and comparative erosion studies of surrounding landforms can indicate the erosive behaviour of waste repositories, only future investigations of capped waste repositories will provide the evidence for their long-term stability. It is a fact that fundamental geological processes such as erosion eventually result in the leveling of any topographic highs. If significantly elevated dumps and dams are constructed in high rainfall, erosive regimes, it is certain that the dry covers will not protect the man-made highlands from erosion in the long term.

6.8
Mine Water

Water management at uranium mine sites follows the general principles of water management at all mine sites (Sec. 3.11). These principles require the containment and disposal of contaminated water in a manner that does not impact on the environment. The release of water from uranium mine sites has to conform with statutory directives. These directives commonly state that the quality of any discharged water has to meet a specified standard which includes maximum acceptable uranium and other radionuclide levels. Water management is to ensure that water courses, aquifers, soils, sediments, irrigation crops, farm animals, and aquatic life are not contaminated by radionuclides, heavy metals, metalloids, sulfate, process chemicals, and other contaminants.

Water management is achieved through collection and disposal. Water is collected from open pit or underground workings, mills, hydrometallurgical plants, waste rock dumps, heap leach piles and ore stockpiles, and channelled into retention ponds (Fig. 6.8). Uncontaminated water can be disposed of by evaporation, land irrigation or discharge whereas contaminated water requires treatment prior to discharge.

6.8.1
Constituents

Waters of uranium mine sites have highly variable compositions, yet they are generally characterized by elevated uranium and thorium levels and their decay products (Ra-226, Rn-222, Pb-210, etc). Some radionuclides found in water such as Ra-226 also originate from natural sources, in particular from the leaching of minerals other than uranium ore minerals. Metal and metalloid concentrations (e.g. As, Be, Cr, Fe, Ni, Se) may be elevated, and oxidation of abundant iron sulfides in mine wastes can lead to AMD development and long-term low pH waters. The geochemical behaviour of radionuclides, metals and metalloids in mine waters is strongly pH and Eh dependent. Enhanced dissolution of radionuclides and heavy metals occurs in acid, oxidized waters.

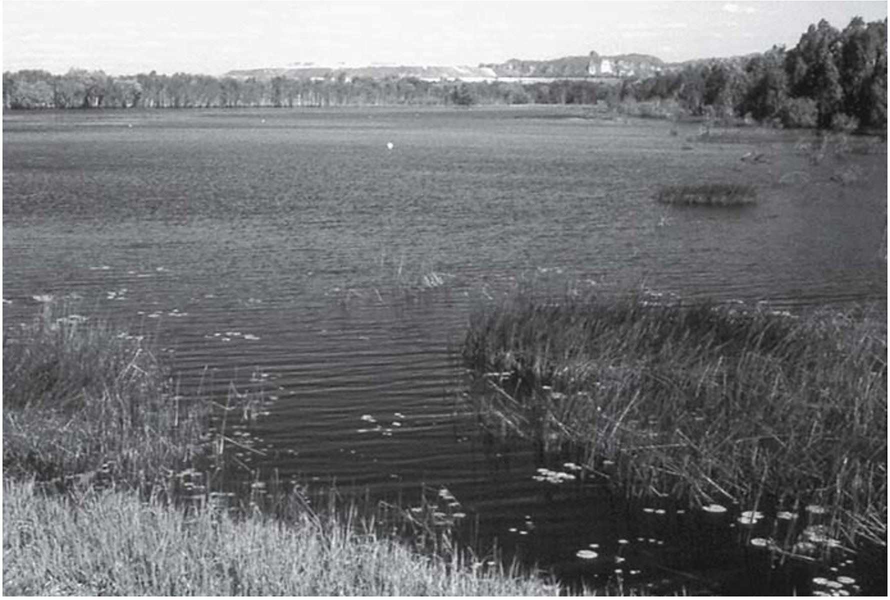

Fig. 6.8. Water retention pond at the Ranger uranium mine, Australia. Waste rock dumps are present beyond the pond

Various process chemicals are used in the hydrometallurgical extraction of uranium (cf. Sec. 6.5). These include sulfuric acid, sulfates, carbonates, chlorides, calcium oxide, magnesium oxide, sodium hydroxide, potassium permanganate, copper sulfate, cyanides, manganese oxides, nitrogen compounds (e.g. ammonium, ammonia, nitric acid), and organic solvents (e.g. kerosene, alcohols). Hence, spent process waters of processing plants tend to have elevated radionuclide, metal, metalloid as well as sulfate, carbonate, chloride, calcium, magnesium, sodium, manganese and nitrogen levels (e.g. NO_3^-, NH_3, NH_4^+).

6.8.2
Treatment

At uranium mine sites, treatment of surface or ground water may be needed because the water is contaminated with radionuclides, metals, metalloids, acid and/or process chemicals. Various methods are available to remove these contaminants from the mine waters. Land irrigation, neutralization, wetlands, radium removal, pump-and-treat, and in situ bioremediation are some of the techniques available to reduce dissolved contaminant values to acceptable levels:

- *Land irrigation.* Uranium mines in tropical regions with high rainfalls must collect, contain and dispose large volumes of contaminated water in a manner which does not impact on the environment. Excess water at such uranium mining operations has been sprayed onto land application areas (Willett and Bond 1995, 1998; Brown et al. 1998). The soils of the land application areas have to possess adsorptive capacities which retain the contaminants. In particular, soils enriched in iron oxides and organic matter are capable of adsorbing significant concentrations of uranium. Other radionuclides (e.g. Ra-226, Pb-210) are also strongly adsorbed by surface soils in irrigation areas and do not reach the regional aquifers and surface waters (e.g. Willett and Bond 1995, 1998). The radionuclides will remain in the surface soils and do not leach into ground waters. However, such a disposal method has several disadvantages. The topsoil is subject to wind and water erosion, represents the substrate for plants, and may be ingested by animals (Willett and Bond 1998). Furthermore, conservative, non-reactive ions such as sulfate, nitrate, manganese, magnesium, and calcium may migrate into the local aquifer and surface waters (Brown et al. 1998). As a consequence, the application of excess water to an irrigation area will result in soil and ground water contamination and subsequent stress to and dieback of local vegetation.

- *Neutralization.* The acidity of uranium mine waters is either due to AMD development or due to the use of sulfuric acid during uranium extraction. Acid, metal-rich (e.g. Cd, Cu, Mn, Mo, Ni, Zn) mine waters can be treated using the same treatment techniques as applied to AMD waters (Sec. 3.12). The chemical treatment of acid, uranium-rich waters with carbonate and lime will reduce dissolved uranium and heavy metal concentrations and neutralize the acidity (Applegate and Kraatz 1991; Fernandes et al. 1998). Dissolved metals and radionuclides precipitate as sludges, and the sludges need to be disposed of in a waste repository which commonly is the tailings storage facility. On the other hand, chemical treatment of acid, uranium-rich waters with carbonate may promote the undesired desorption, mobilization and leaching of uranium from mine wastes. Dissolution of solid carbonate generates bicarbonate ions, and the uranyl ions are able to complex with the bicarbonate ligands. Consequently, excessive addition of carbonate to uranium mine wastes and contaminated soils can enhance uranium mobility and exacerbate existing contamination problems (Elles and Lee 1998; Wanty et al. 1999) (cf. Sec. 3.12.1).
- *Wetlands.* Wetlands are successfully used to treat waters with elevated uranium and radium concentrations. Wetlands have abundant clays, organic matter, algae, bacteria, fungi, and lichens which are effective in removing dissolved contaminant concentrations (Noller et al. 1997; Haas et al. 1998). Much of the uranium is adsorpted onto the organic-rich wetland sediments, or the reducing conditions convert the mobile U^{6+} to the immobile U^{4+} species and cause the precipitation of uranium in the wetland substrate.
- *Radium removal.* The removal of radium from water is accomplished by precipitation with barium chloride. Barium chloride is introduced into the water circuit, and the radium will coprecipitate with barium sulfate as illustrated by the following reaction (Benes et al. 1983):

$$BaCl_{2(s)} + Ra^{2+}_{(aq)} + SO^{2-}_{4(aq)} \rightarrow 2\,Cl^{-}_{(aq)} + (Ba,Ra)SO_{4(s)} \qquad (6.10)$$

Any calcium present will precipitate as calcium sulfate crystals. Settling and filtration of the precipitated salts follow in constructed ponds. Ponds should be lined to prevent contamination of ground waters with radionuclides. Evaporation of waste waters in ponds lead to the precipitation of salts and sediments. The radioactive salts and evaporation pond sediments cannot be left in the treatment ponds otherwise they redissolve. The salts and sediments are generally placed with the tailings into a tailings storage facility.

Contaminated ground water may be treated using ex situ (e.g. pump-and-treat) or in situ treatment techniques (e.g. bioremediation, permeable reactive barriers):

- *Pump-and-treat.* The pump-and-treat method aims to capture the impacted ground water plume. A number of extraction wells pump the contaminated ground water to the surface. This technique relies on the extraction of uranium and other contaminants with the water and on fast desorption if the contaminants are adsorpted onto the host rock in the polluted aquifer (Abdelouas et al. 1998a,b). Following extraction of the contaminated ground water, the water is treated using separation processes such as ion exchange, reverse osmosis, biosorption, bioreduction, bioaccumulation, and reductive precipitation of uranium (Abdelouas et al. 1999).
- *In situ bioremediation.* In situ bioremediation is based on the injection of nutrients and/or specific bacteria into the aquifer (e.g. *Desulfovibrio, Geobacter metallireducens, Shewanella putrefaciens, Colstridium* sp.). The bacteria precipitate the dissolved uranyl complexes as insoluble uranium oxide through the following processes: (*a*) incorporation of uranium into cell structures; (*b*) adsorption of dissolved uranium from solution; and (*c*) direct or indirect reduction of the mobile U^{6+} to the immobile U^{4+} species which precipitates as insoluble uraninite (Suzuki and Banfield 1999; Abdelouas et al. 1998b, 1999, 2000). This latter property of microorganisms – to be able to reduce U^{6+} to the immobile U^{4+} – is used in the remediation of uranium contaminated ground waters. Direct reduction of the mobile U^{6+} to the immobile U^{4+} species can be performed by particular microorganisms. Indirect reduction of U^{4+} may be caused through the proliferation of sulfate-reducing bacteria, which in turn lead to reducing conditions in the uraniferous ground waters. Both direct and indirect reduction result in the precipitation of dissolved U^{6+} as insoluble U^{4+} oxide.
- *In situ permeable reactive barriers and reactive zones.* In situ permeable reactive barriers (PRB) and reactive zones (RZ) are based on the placement of solid reactive materials into the contaminated ground water. The application of permeable reactive barriers requires excavation of a trench, placement of the reactive materials into the trench, and backfilling; hence, the technique is limited to shallow aquifers. By contrast, the reactive zone technology uses injection points perpendicular to the ground water flow. Reducing materials like metallic iron can be employed to retain uranium and radium on solid particles (Burghardt and Kassahun 2005).

6.9
Monitoring

Waste rock dumps, tailings dams, and heap leach piles are potential sources of radionuclides, acid, salts, heavy metals, and metalloids. These sources need mineralogical, geochemical and radiochemical characterization. Uranium concentrations in solid mine wastes can be determined using a range of analytical methods whereas uranium mineral identification is primarily achieved through X-ray diffraction (Wolf 1999; Hill 1999). Radionuclide concentrations are established using alpha and gamma-ray spectrometry whereas radon gas concentrations are investigated using radon emanometry (Nielson et al. 1991; Sharma 1997).

Kinetic tests are commonly applied to simulate the weathering and oxidation of sulfidic waste samples. The tests expose sulfidic waste over time, from several months to several years, to moisture and air (Sec. 2.7.4.2). The field or laboratory based experiments are also used to investigate the leaching behaviour of uranium mine wastes. The uranium mine wastes are placed into field bins or columns and subjected to periodic or continual leaching in order to simulate the addition of ground or surface waters. The wastes require mineralogical, geochemical and radiochemical characterization prior to and after leaching. The leachates are monitored for water quality parameters (e.g. pH and EC) and analyzed for their chemical and radiochemical composition. Data from such experiments can be used to evaluate acid production and the migratory behaviour of radionuclides, heavy metals, and metalloids over time.

Environmental monitoring of uranium mine sites include periodic chemical and radiochemical measurements of ground and surface waters, stream sediments and soils. In addition, aquatic biota (e.g. fish) are investigated for their radiochemical composition to detect uptake of radionuclides by aquatic organisms. Mosses and lichens are often used to monitor air contaminants as these rootless organisms reflect atmospheric fall-out rather than substrate chemistry (Ripley et al. 1996). Atmospheric measurements of radon gas and dust particles are an integrated part of the monitoring program. In particular, geochemical analyses of waters and stream sediments are very useful for the identification, monitoring, control, and evaluation of environmental impacts in the aquatic system (Noller and Hart 1993). The migratory behaviour of dissolved uranium and other from contamination sources into aquifers can be modelled using computational software, including mass transport models (e.g. MODFLOW) and geochemical speciation programs (e.g. HARPHRQ).

The environmental risks of uranium mine wastes will last until the radioactivity of the mine wastes has decreased to acceptable levels. Therefore, operating and rehabilitated uranium mine sites require monitoring and periodic environmental reviews well beyond mine closure and for at least 1 000 years (i.e. the engineered life-span of tailings repositories).

6.10
Radiation Hazards

A low level of radioactivity is part of the natural environment (Eisenbud and Gesell 1997; Ewing 1999; Gaines 2000). Naturally occurring background levels of radiation originate from cosmic radiation, the radioactive decay products of radon in the air, and the natural radioactivity of the ground. Much of the radioactivity of rocks and minerals is due to the decay of uranium (i.e. U-238, U-234), thorium (i.e. Th-232), their radioactive decay products as well as the decay of the potassium isotope K-40. The abundance of uranium, thorium and potassium varies in different rock types and minerals (Sharma 1997). Hence, the natural radiation dose varies depending on the geological ground above which and altitude at which people live. Radioactivity is also present in water, air, plants, food, and even internally within the human body (Kathren 1998; Ewing 1999). Radiation is unavoidably received by humans and for the great majority of the population, exposure to natural radiation exceeds by far that from artificial, medical and occupational sources.

6.10.1
Radiation Dose and Human Health

Radioactive nuclides of the U-238, U-235 and Th-232 series emit ionizing radiation in the form of alpha and beta particles as well as gamma-rays. Animals and humans get exposed to this radiation through: (*a*) external radiation emitters; and (*b*) ingestion or inhalation of radionuclides. Very high concentrations of radionuclides may be acquired through the foodchain whereby terrestrial or aquatic plants obtain radionuclides from contaminated air, water and soil. The radionuclides get into organisms using the transport mechanisms of nutrient ions, so the radionuclides become concentrated in the foodchain. For example, Ra-226 follows the pathways of calcium. The radionuclide accumulates in calcium sinks such as bones and continues to emit ionizing radiation.

It is established that work with radioactive materials carries with it an increased risk of tissue damage including radiation induced cancers, leukemia, and genetic mutations. Radiation protection standards assume that any dose of radiation – no matter how small – involves the possibility of risk to human health. Ionizing radiation can be particularly harmful if a large enough dose is received (Table 6.5). While small radiation doses such as medical X-rays are not capable of causing radiation sickness or death, they slightly increase the risk of cancer several years after the exposure has occurred. As more is known about the effects of ionizing radiation, the dose levels considered to be safe have been revised. Radiation exposures for the general public and in the workplace have been lowered over the years, and the occupational maximum permissible radiation exposure level has dropped to about one tenth of that considered safe in the early 1950s.

The health effects of radon exposure are still debatable, and the effects of low level radiation dose on cells are still to be determined. While exposure to excessive radiation is a health hazard and may even lead to death, a small radiation dose may be beneficial for the cure of various ailments. There is a practice of radon consumption and inhalation by the general public in certain parts of the world. In Germany, Austria and Poland, mineral waters and underground mines with known high levels of radon are successfully used for the treatment of various ailments (Kathren 1998). The consumption of radon bearing mineral waters and the inhalation of radon-rich air appear to have a beneficial effect. Will decommissioned uranium mine sites and other non-uranium mines with high radon levels have a future as sanatoriums and health spas?

The radiation dose to members of the public from operating uranium mines is in most cases negligible as access to the mine sites is controlled and occupation of the mining areas by the general public is zero. In populated areas, however, environmental dust and radon monitoring programs have to be implemented around uranium mine sites. Direct radiation and ingestion as well as inhalation pathways need to be evaluated as well. The potential for significant radiation exposure especially exists for mine staff.

6.10.2
Occupational Radiation Exposure

Much of the occupational radiation exposure at uranium mine sites does not originate from the decay of uranium isotopes but from the decay products of U-238 and

Table 6.5. Comparative radiation doses and likely effects of radiation doses to the human body (Ripley et al. 1996; Uranium Information Centre 2001b,c; Major 2001)

Radiation dose		Effects of radiation dose
10 000	mSv in a short term dose	Immediate illness and subsequent death
1 000	mSv in a short term dose	Temporary illness; likelyhood of cancer
750	mSv per year	Mean annual radiation dose to East German miners from 1946 to 1954, resulting in thousands of cases of lung cancer (cf. Case Study 6.1)
350	mSv in lifetime	Criterion for relocating people after the 1986 Chernobyl accident
100	mSv per year	No evidence for increased cancer risk or immediate effects below this level
20	mSv per year av. over 5 years	Occupational maximum permissible exposure level for nuclear industry employees and uranium miners (International Commission on Radiological Protection)
5.2	mSv per year	Average dose to employees at the Ranger uranium mine, Australia
4–5	mSv per year	Average dose to Australian uranium miners
5	mSv	Abdominal X-ray
3	mSv per year	Typical background radiation to North American public
2.9	mSv per year	Average occupational dose to United States nuclear industry employees
2.7	mSv per year	Average dose to underground employees of the Olympic Dam uranium mine, South Australia
2	mSv per year	Typical background radiation to Australian public
1.1	mSv per year	Average dose to Canadian uranium refinery workers
1	mSv per year	Maximum permissible exposure level for general public above that received from background and medical exposure (International Commission on Radiological Protection)

U-235 (i.e. Ra-226, Rn-222). While uranium isotopes are radioactive, the isotopes U-238 and U-235 have very long half-lifes and uranium is not strongly radioactive. On the other hand, both uranium isotopes emit alpha particles. The release of alpha particles is a potential hazard if the uranium occurs in fine-grained material. The finer grain size results in larger surface areas and greater release of alpha particles from the material. Alpha particles cannot penetrate the skin and are only a potential hazard if they are inside the human body. Consequently, the handling of solid uranium concentrate at mine sites is not so much a radioactive hazard but a potential inhalation or ingestion hazard. Uranium itself is a suspected human carcinogen and has a chemical toxicity (Wanty et al. 1999). The inhalation or ingestion of uranium can be prevented using appropriate ventilation, protective clothing, and strict hygiene standards.

The prime health hazard – during uranium mining and after mine closure – relates to ionizing radiation and the carcinogenic properties of radionuclides (e.g. Ra-226) and radon (Rn-222) gas. Employees of uranium mines can be exposed to radiation and radon gas via four principal exposure pathways (Table 6.6):

- *Direct external radiation from uranium ores, tailings and waste rocks.* Employees will be exposed to external radiation in the form of gamma-rays as well as alpha and beta particles emitted by isotopes of the U-238, U-235 and Th-232 series.
- I*ngestion of contaminated water.* Leaching of wastes can carry radioactive nuclides, metals, and metalloids to surface and ground waters. Thus, ground and surface water within or near the mine site can contain elevated levels of dissolved radioactive isotopes and should not be used as drinking water.
- *Inhalation of radon.* Radon-222 gas emanates from ores, wastes, and tailings and may be inhaled by employees. Airborne radionuclides, particularly Rn-222, may impact on the health of humans, because Rn-222 and its radioactive decay products deliver an internal radiation dose to the lungs.
- *Inhalation and ingestion of dust containing radioactive isotopes.* At uranium mine sites, atmospheric emissions are not restricted to radon gas. All mining, tipping, handling, transport, crushing and milling operations produce dust. In addition, dry uncovered tailings can be a source of radioactive dust particles. The ore or tailings dust contains radioactive isotopes of the U-238, U-235 and Th-232 series, and the dust may be inhaled and ingested by employees.

Uranium mine wastes emit very low to elevated levels of radiation and variable levels of radon gas. Today, low level radiation doses for employees can be achieved through (Table 6.6):

- *Installation of covers.* The release of Rn-222 to the atmosphere from tailings is major pathway of radon exposure at uranium mine sites. A reduction in radon emanation from tailings repositories is generally achieved by installing cover materials. At operating uranium mines, tailings are commonly covered with water which reduces radiation levels. Where tailings are collected and kept wet under permanent water cover, the radon flux is reduced to only 1% of the radon flux from dry tailings (Davy and Levins 1984). Wet or dry covers on tailings and other wastes need to be of at least 30 cm thickness in order to reduce radiation levels to background levels.
- *Dust suppression.* The inhalation and ingestion of radionuclides contained in dust need to be minimized as radionuclides emit gamma-rays and alpha particles. Dust suppression can be achieved by wetting and covering the potential dust sources.
- *Appropriate ventilation.* Uranium mine sites are always monitored for levels of radon gas that is released during the natural radioactive decay of uranium. Ventilation generally reduces radon gas levels, however, in some mines the radiation and radon levels are so high that mining must be done with remote control equipment and robots. Natural ventilation in an open cut mine removes radon gas whereas an underground uranium mine requires an engineered ventilation system. Forced ventilation reduces radon and radon daughter exposure.
- *Radiation dose monitoring.* Personal radiation doses are monitored to limit the radiation exposure of individual employees.
- *Strict hygiene standards, ventilation, and protective clothing.* Employees handling uranium concentrate have to adhere to strict hygiene standards and have to work in protective clothing in appropriately vented environments. This will minimize the ingestion, adsorption and inhalation of uranium.

Table 6.6. Potential occupational hazards at uranium mining and processing sites and their management (after Davy and Levins 1994; OECD 1999)

Hazards	Sources	Possible contaminants	Management
External radiation	Mine workings, ore stockpiles, tailings repository, waste rock dumps, processing plant	Gamma-rays, alpha and beta particles	Monitoring of personal radiation doses; engineered ventilation system
Ingestion of surface or ground water	Water within or near the mine site	Dissolved radionuclides	Inappropriate drinking water supply
Inhalation of radon	Mine workings, ore stockpiles, waste rock dumps, processing plant	Radon-222	Monitoring of personal radiation doses; engineered ventilation system
Inhalation of radon	Tailings repository	Radon-222	Wet cover during operation; dry or wet cover once disposal ceases
Inhalation of dust containing radioactive isotopes	Working areas with mining, blasting, crushing, and screening; wind erosion of ore and waste rock piles and tailings	Radionuclides, silica dust	Forced ventilation in underground mines; wetting of working areas; wind resistant covers for ore and waste piles; collection of dust using filters; dust suppression using wetting and covering of potential dust sources
Inhalation, skin adsorption or ingestion of uranium	Packaging of uranium concentrate	Uranium	Ventilation; air hoods; filters; protective clothing; hygiene

The above protection measures ensure that radiation doses are below recommended dose limits and are as low as reasonably achievable. In the past, little attention was paid towards proper ventilation of underground mines, dust suppression, and the radiation exposure of mine workers. An example for this is the Radium Hill uranium mine in South Australia. The mine operated from 1952 to 1961 (Fig. 6.6). The frequency of lung cancer deaths in the former Radium Hill workforce is associated with duration of work underground and cumulative exposure to radon (Woodward and Mylvaganam 1993). In contrast, modern underground uranium mines are far ore strictly controlled and far better ventilated. Furthermore, in industrialized nations, health standards have been set for the exposure to gamma radiation and radon gas.

6.11
Environmental Impacts

Many uranium ores were exposed to the surface prior to mining. At these sites, there was natural release of radioactivity into the environment as well as natural dispersion of uranium and other elements into soils, plants and creeks prior to mining. Plants may adapt to uranium-rich soils. In fact, plants growing on naturally radioactive places are known to absorb so much Ra-228 that the plants produce an image when placed on photographic film. Also, ground waters in contact with uranium ores are often naturally radioactive and too saline for human and animal consumption. Thus, natural dispersion of radionuclides, metals and metalloids is known to occur from uranium ores into surrounding soils, waters, plants, and stream sediments.

Mining, processing and metallurgical extraction of uranium ore may impact on air, soil, sediment as well as surface and ground water unless suitable waste disposal and rehabilitation strategies are adopted (Table 6.7, Case Study 6.2). The following environmental problems are encountered with uranium mine wastes:

- *Excessive radioactivity levels and radon emissions.* The escape of radon and radionuclides from waste repositories may be possible due to non-existent or inadequate covers. Uncovered tailings are exposed to erosion, and windblown radioactive dust and erosive products are dispersed from the storage facility into the surrounding soils, sediments, and waters. Intrusion of plant roots and burrowing animals through cover materials into the wastes can provide pathways for infiltrating surface water and cause the upward migration of radionuclides and the release of radon.
- I*nappropriate use of tailings and waste rocks.* At some historic uranium mine sites, tailings and crushed wastes have been used for landscaping purposes, for the production of gravel and cement, and for the construction of houses, roads and railway beds. As a consequence, wastes with elevated levels of uranium and radioactivity have been dispersed over large areas and along transport corridors, and homes constructed with uranium mine wastes exhibit high radon and gamma-ray radiation levels.
- *Failure of tailings dams.* Rehabilitated or operating tailings dams may fail to contain the tailings and release them to the environment through: liquefaction; rapid increase in dam wall height; foundation failure; excessive water levels; or excessive seepage (cf. Sec. 4.3.3). There have been several uranium tailings dam leakages, discharges and failures since the 1950s. The largest single release of uranium tailings ever occurred in the region of the upper Puerco River of New Mexico, United States (Landa and Gray 1995). In this area, uranium mines were dewatered, and the effluent was released to the local river for over 22 years. In 1979, a tailings dam pond failed, resulting in the release of uranium tailings. An estimated 360 000 m^3 of tailings liquid and 1 000 t of tailings solids were discharged. The tailings liquid had a pH value of 1.6, and the total gross-alpha activity was estimated to be 130 000 pCi l^{-1} which is approximately 10 000 times higher than drinking water quality guidelines. Twenty years after the spillage, the tailings pond spill and the uncontrolled release of mine waters were still discernible as indicated by uranium contamination of the Puerco River as far as 70 km downstream from the mines (Landa and Gray 1995).
- *Soil and sediment contamination.* Failure of tailings dams, unconstrained erosion of waste repositories, and improper disposal of contaminated water from mining, mineral processing, and metallurgical operations may release contaminants into local environments (Case Study 6.3). If mine waters are released into local stream systems, the environmental impact will depend on the quality of the released effluent. The release may cause soils, floodplain sediments, and stream sediments to be become contaminated with radionuclides, metals, metalloids, and salts (Pinto et al. 2004). The metals and metalloids may be contained in various sediment fractions, including the

Table 6.7. Potential environmental impacts at uranium mining and processing sites and their treatment and management (after Davy and Levins 1994; OECD 1999)

Environmental impacts	Sources	Possible contaminants	Treatment and management
Excessive radioactivity levels	Waste rock dumps, tailings repository	Radon, radionuclides	Construction of engineered waste repositories to reduce radon release and radioactivity levels
Erosion of tailings cover materials and wastes	Waste rock dumps, tailings dams	Radionuclides, metals, metalloids, acid, process chemicals	Wet cover during operation; dry or wet cover once disposal ceases
Failure of tailings dams	Tailings dams	Radionuclides, metals, metalloids, acid, process chemicals	Construction of waste repositories for the long term
Ground and surface water contamination (drainages and seepages)	Ore stockpiles, waste rock dumps, tailings repository, processing plant	Radionuclides, metals, metalloids, acid, process chemicals	Collection of seepage and run-off waters for treatment or reuse in mineral processing; construction of waste repositories to limit water infiltration: (*a*) clay or synthetic liners to seal the floor of the waste storage facility; and (*b*) clay to cap tailings storage facility
Ground and surface water contamination (process water)	Processing plant	Radionuclides, metals, metalloids, acid, process chemicals	Neutralization of acidity and precipitation of heavy metals by adding lime or limestone; precipitation of Ra-226 by adding barium chloride; recycling to reduce volume
Ground and surface water contamination (AMD)	Sulfidic ore stockpiles, waste rock dumps, tailings dams	Acidity, metals, metalloids, radionuclides	Clay or synthetic liners to seal the floor of the waste storage facility; wet or dry cover on waste storage facility; collection of AMD water for treatment
Atmospheric emissions	Sulfuric acid production plant	Sulfur oxides, sulfuric acid mist	Demister, scubbers, tall stacks

adsorptive, iron and manganese hydroxide, carbonate, organic, and residual silicate fractions.

- *Ground and surface water contamination.* In the past, untreated mine waters have been released accidentally or deliberately into local rivers and lakes. In addition, unconstrained seepage and run-off waters have mobilized and transported contaminants from waste rock dumps, tailings dams or ore stockpiles into local creeks and aquifers. Thus, ground and surface water contamination may originate from tailings dams, waste rock piles, evaporation ponds, and contaminated soils (Pinto et al. 2004). In particular, water may leak from tailings impoundments into underlying aquifers if the waste repositories are uncapped, unlined and permeable at their base (Zielinski et al. 1997). At such sites, significant concentrations of uranium and other contaminants have been found in ground water plumes migrating from the uranium tailings impoundments. If not rectified, the plumes of contaminated water will migrate over time downgradient, spreading beyond the waste repositories, surfacing at seepage points, and contaminating surface waters. The migration rate of plumes is highly

Case Study 6.2. Environmental Review of the Rehabilitated Mary Kathleen Uranium Mine, Australia

Mining and Rehabilitation at Mary Kathleen

The Mary Kathleen uranium deposit was discovered in 1954, mined in 1956–1963 and 1976–1982, and subsequently rehabilitated (Flanagan et al. 1983; Ward et al. 1983, 1984; Ward and Cox 1985). The aim of rehabilitation was to leave the site in a safe and satisfactory condition consistent with future land use in the area (i.e. cattle grazing), requiring no foreseeable on-going maintenance and a minimum of precautionary monitoring (Ward et al. 1983, 1984; Ward and Cox 1985). All areas were to be made safe for public access, and radiation and radon daughter levels were to be within acceptable limits. Rehabilitation of the site was completed in 1985 at a cost of some A$19 million. The work won an award for environmental excellence from the Institute of Engineers Australia in 1986. In 1999 and 2000, gamma-ray data, plus stream sediment, soil, rock chip, mineral efflorescence, vegetation and water samples were collected from selected sites to assist in the examination of the current environmental status of the rehabilitated area (Lottermoser and Ashley 2005a; Lottermoser et al. 2005).

Open Pit

Elevated gamma-ray readings in the open pit correspond to exposed ore lenses, the former haul road, and abandoned ore stockpiles (up to 16 mSv per year). Surficial oxidation of ore and adjacent sulfide-bearing rocks has led to contemporary precipitation of mineral efflorescences on the pit walls. Wallrock oxidation of reactive sulfides (mainly pyrrhotite breakdown) produces acidic solutions, yet buffering reactions of these fluids with gangue calc-silicates and carbonate phases prevent low pH conditions from developing. The open pit lake contains saline surface waters at a pH of 6.11.

Waste Rock Piles

Waste rock piles are up to 30 m thick and have been covered by a thin veneer of benign waste. However, there are high radiation levels on several waste rock piles (up to 20 mSv per year) which were only partly covered or were ripped for seeding after the thin cover was put into place. Biogeochemical analyses indicate that *Enneapogon lindleyanus* (grass), *Cymbopogon bombycinus* (grass), *Aerva javanica* (kapok bush), *Aristida longicollis* (poaceae) and *Acacia chisholmii* (wattle) accumulate certain elements (As, Ce, Cu, La, Ni, Pb, Th, U, Y, Zn) at mined and disturbed areas compared to background sites. Stream sediments – accumulating below waste rock piles – are enriched in copper, zinc, arsenic, nickel, lanthanum, cerium, and uranium, indicating active weathering and erosion of waste materials into the local drainage system.

Tailings Dam

The tailings disposal system consisted of a tailings dam (0.28 km^2) and a series of evaporation ponds (0.6 km^2). The tailings dam contains 7.1 Mt of un-neutralized tailings. The dam was formed by constructing a rolled earth fill and metasedimentary waste rock embankment across a narrow section of a small valley. It was constructed without a basal liner. In 1982, kinetic testing of the tailings indicated that the leachate from the tailings dam would contain low radionuclide, heavy metal and acidity levels. Studies concluded that the composition of leachates from the tailings dam would largely be controlled by gypsum dissolution. Sulfate contamination of the ground water system would be the main environmental impact (Flanagan et al. 1983). The former tailings dam was subsequently rehabilitated using a multi-barrier system (i.e. clay and waste rock layers).

variable and dependent on the physical and chemical characteristics of the aquifer or waste material. The contaminated ground water may not only contain elevated uranium but also high sulfate, nitrate, heavy metal and metalloid concentrations as well as elevated salinities and TDS values (Lawrence et al. 1997; Abdelouas et al. 1998a).

Case Study 6.2. *Continued*

Today, gamma-ray measurements demonstrate an intact tailings dam cover. Nevertheless, seepage of acid (pH 5.71), saline (0.31%) waters occurs from the toe of the tailings dam into the evaporation ponds and local drainage system. The sulfate concentration of the seepage water (4.2 g l^{-1}) is well below that of the discharge water from the former mill (21 g l^{-1}) and that of the tailings liquid before rehabilitation (24 g l^{-1}). Hence, acid-producing reactions are sufficiently buffered within the tailings storage area, yet there is dissolution of solid phases within the repository. Seepage waters are calcium-, sulfate-rich with elevated iron, manganese, nickel, uranium and zinc values. The seepage waters precipitate abundant sulfate efflorescences and iron oxyhydroxide ochres. These precipitates exhibit elevated radiation and major (i.e. >1 wt.%) concentrations of Fe, S and Ca, minor contents (i.e. >1 000 ppm) of Ce, La, K, Mg, Mn, and Na, elevated (i.e. >100 ppm) contents of U, and traces (i.e. <100 ppm) of As, Ba, Cu, Ni, P, Pb, Sr, an Th.

Drainage

Seepage of saline waters occurs from the tailings dam and evaporation ponds into the local creek via surface and subsurface flows as indicated by salt-encrusted creek banks. This stream and its tributaries are usually active only in the wet season. At other times, few permanent water holes exist although there is some sustenance of flow from the tailings dam seepage. When sampled during the dry season, pools in the creek system are shallow, saline (up to 3%), alkaline (up to pH 8.6), and strongly enriched in sulfate (up to 26 g l^{-1}) and uranium (up to 5 mg l^{-1}). The pools locally sustain fish and reeds in lower salinity regimes.

Conclusions

The environmental assessment of the rehabilitated Mary Kathleen uranium mine has revealed the following features:

1. Radiation levels are below acceptable limits.
2. The tailings dam structure and its cover are intact.
3. No exposure pathway to radiation has been identified that could pose a threat to human health or other life forms.
4. Uncovered or partly covered, steeply sided, thick waste rock dumps continue to shed dissolved and particulate contaminants into local soils, sediments, and waters.
5. In 1984, at the time of mine closure and mine site rehabilitation, scientists of the Australian Nuclear Science and Technology Organisation predicted that AMD and radionuclide mobility from the tailings dam would not be a problem and that the tailings had a high capacity to neutralize acid. This investigation has confirmed that AMD generation does not occur. However, there is dissolution of solid phases within the tailings dam, and radionuclides are mobilized from the waste repository into surface water seepages.
6. Similarly at the time of closure, it was predicted that uranium and heavy metals would be adsorbed within the tailings. They would not be leached from the tailings dam into the environment. However, metal (Fe, Mn, Pb, Th, U, Y), metalloid (As), alkali (Ca, Mg, Na, K, Sr, Ba), rare earth element (La, Ce), radionuclide and sulfate mobilization occurs from the tailings storage area into surface water seepages.
7. Saline subsurface and surface waters flow from the tailings dam and the evaporation ponds into the local creek system causing its salinization during the dry season. The saline water is accessible to cattle.

Natural attenuation processes in aquifers can reduce the constituent concentrations to background levels in the pathway of the subsurface drainage (Erskine et al. 1997; Schramke et al. 1997) (cf. Sec. 3.12.6). For example, reducing environments in the ground water will limit the migration of redox sensitive elements (e.g. U, Se, Cr). Also, neutralizing minerals including carbonates may be contained in the aquifers, and these minerals buffer acid ground waters (Fig. 3.9). The neutralizing minerals will

Case Study 6.3. Environmental Review of the Rehabilitated Radium Hill Uranium Mine, South Australia

Introduction

The evaluation of rehabilitated mine sites is a challenging task because most rehabilitated mine sites represent very young landforms (i.e. less than 20 years old), which have not achieved equilibrium with the surrounding environment. Leaching processes, AMD development and physical erosion are all kinetic processes; processes which require time. Therefore, rehabilitated mine sites should not be evaluated immediately post mining and post remediation.

Recent research on rehabilitated uranium mine sites located in wet climates has revealed the varied success of the applied rehabilitation efforts (e.g. Menzies and Mulligan 2000; Peacey et al. 2002; Ritchie and Bennett 2003). In wet and seasonally wet climates, AMD development and the leaching of waste repositories are dominant pathways of contaminants into surrounding environments. In comparison, there is little knowledge of the status and environmental impacts of rehabilitated uranium mines in dry climates. To date, the few studies conducted on rehabilitated uranium mine sites in semi-arid and arid climates have largely focussed on uranium mill tailings repositories and related ground and surface water investigations.

The Radium Hill Mine

The Radium Hill uranium deposit, in semi-arid eastern South Australia, was discovered in 1906 and mined for radium between 1906 and 1931 and for uranium between 1954 and 1961 (production of 969 300 t of davidite ore averaging 0.12% U_3O_8). In the 1980s, rehabilitation was limited to removal of mine facilities, sealing of underground workings and capping of selected waste repositories. In 2002, gamma-ray data and samples of tailings, uncrushed and crushed waste rock, stream sediment, topsoil and vegetation were collected to assist in examination of the current environmental status of the mine site (Lottermoser and Ashley 2005b).

Physical Dispersion

The data indicate that capping of tailings storage facilities did not ensure the long-term containment of the low-level radioactive wastes due to the erosion of sides of the impoundments. Moreover, wind erosion of waste fines (phyllosilicates, ore minerals) from various, physically unstable waste repositories has caused increasing radiochemical (from a background dose of 35–70 nSv hr^{-1} to max. 940 nSv hr^{-1}) and geochemical (Ce, Cr, La, Lu, Rb, Sc, Th, U, V, Y, Yb) impacts on local soils. Plants (saltbush, pepper tree) growing on waste dumps display evidence of biological uptake of lithophile elements, with values being up to 1–2 orders of magnitude above values for plants of the same species at background sites. However, radiation doses associated with the mine and processing site average 670 nSv hr^{-1}; hence, visitors to the Radium Hill site will not be exposed to excessive radiation levels. Although rehabilitation procedures have been partly successful in reducing dispersion of U and related elements into the surrounding environment, it is apparent that 20 years after rehabilitation, there is significant physical and limited chemical mobility, including transfer into plants. Additional capping and landform design of the crushed waste and tailings repositories are required in order to minimize erosion and impacts on surrounding soils and sediments.

be eventually consumed, and the acid ground water plume will migrate further downgradient. Such contaminated ground water requires treatment (cf. Sec. 6.8.2).

- *Acid mine drainage.* Uranium ores which contain abundant iron-rich sulfides may oxidize upon exposure to the atmosphere, and AMD may develop in mine workings or mining, processing and metallurgical wastes. The problems of AMD and elevated levels of dissolved radionuclides are linked. Low pH, oxygenated waters dissolve uranium ore minerals and sulfides, and radionuclides and metals are mobilized into ground and surface waters.

6.12
Summary

Radioactivity is the issue which sets uranium mine wastes apart from other mine wastes. Uranium commonly occurs in the form of uraninite, brannerite, coffinite, and pitchblende. Much of the radioactivity of uranium ores and wastes is due to the decay of the uranium isotopes U-238 and U-235 and their radioactive decay products. These radionuclides serve as a long-term source of ionizing radiation. Radium-226 and Rn-222 are intermediate daughter nuclides of the U-238 series. They are of most concern in uranium mining, processing, metallurgical extraction, and waste management. Radium-226 is a radionuclide that has: (*a*) a significant half-life of 1 622 years; (*b*) a geochemical behaviour similar to calcium; (*c*) a high radiotoxicity; (*d*) an affinity for accumulating in bones; and (*e*) a high solubility in ground and surface waters. Radium-226 is the source of Rn-222. Radon-222 is a radionuclide that: (*a*) has a half-life of 3.8 days; (*b*) is soluble in water; (*c*) is highly mobile due to its gaseous state and inert chemical properties; and (*d*) decays to radioactive solid daughter products that can be deposited in human lungs.

Mineral processing of uranium ores relies on acid or alkaline leaching. Conventional uranium extraction is based on the leaching of the ore in hydrometallurgical plants or heap leach piles. In situ leach techniques leave the ore in the ground and inject the process chemicals via drill holes into the ore horizon. The process chemicals produce a solution from which uranium is obtained.

Mining, mineral processing and metallurgical extraction of uranium ores result in the production of tailings, mine water, waste rocks, and heap leach residues. Most wastes of uranium mining and processing operations can be classified in terms of radioactivity as non-radioactive or low-level radioactive waste.

Conventional extraction of uranium in a hydrometallurgical plant produces uranium mill tailings. Once the uranium (U-238, U-235, U-234) is recovered from the ore, most of the radioactive daughter nuclides end up in uranium mill tailings. Thus, uranium tailings have special containment requirements because of their radioactivity. Tailings carry about 85% of the radioactivity originally present in the uranium ore.

Uranium tailings contain radionuclides, heavy metals and metalloids as: (*a*) dissolved species; and (*b*) insoluble and potentially soluble solid forms. The potential release of radionuclides, heavy metals, and metalloids from tailings solids and the presence of radionuclides in solution are undesirable. Pore waters laden with contaminants may migrate into aquifers or surface at seepage points. The mobilization of radionuclides, heavy metals and metalloids from tailings solids into the tailings liquids may occur after tailings deposition. Such mobilization can be induced through several factors: (*a*) AMD development; (*b*) presence of process chemicals; (*c*) acid leaching or reduction of iron and manganese oxyhydroxides; (*d*) bacterial reduction; and (*e*) presence of clay minerals. Acid leached tailings tend to contain high concentrations of soluble and dissolved radionuclides, heavy metals and sulfate unless the tailings have been neutralized prior to discharge to the tailings storage facility.

Uranium tailings need to be covered during operation in order to reduce Rn-222 emanation. Finite disposal options for uranium tailings include: (*a*) placing them under water in a lake, ocean or wetland environment; (*b*) backfilling them into a mined-out open pit; and more commonly (*c*) dumping them into a tailings dam. Once mining ceases, uranium tailings repositories require covers, and conventional cover designs are multi-layer barriers. Uranium tailings contain radioactive isotopes with half-lifes exceeding the engineered design and structural life of tailings dams. Therefore, the long-term stability of uranium tailings dams is important in regions with high erosion rates.

Mine water at uranium mine sites is invariably radioactive arising from dissolved U-238, U-235, Th-230, Ra-226 and Pb-210 ions. The water may also contain various heavy metals and metalloids, and some of the heavy metal load can be the result of sulfide oxidation and resulting AMD. Dissolved uranium in oxidized mine water is mainly in the form of the uranyl ion (UO_2^{2+}) which forms complexes with carbonate, sulfate, and other ligands. Uranium can be effectively leached from mine wastes under acid, oxidizing weathering conditions. The uranium will remain in solution until: (*a*) the pH is raised to higher levels; (*b*) coprecipitation or adsorption reactions occur; or (*c*) reducing environments are met. Surface and ground water can be contaminated with radionuclides, metals, metalloids, acid, and process chemicals. Treatment techniques of such contaminated waters include land irrigation, neutralization, wetlands, and radium removal. Contaminated ground water may be treated using ex situ (pump-and-treat) or in situ (bioremediation, permeable reactive barriers) techniques.

Environmental concerns with uranium mining include radiation hazards, in particular to the workforce. Employees of uranium mines can be exposed to ionizing radiation and radon gas via: direct external radiation from uranium ores, tailings and waste rocks; ingestion of contaminated water; inhalation of radon; and inhalation and ingestion of dust containing radioactive isotopes. These radiation hazards can be minimized and low level radiation doses can be achieved through: installation of covers; appropriate ventilation; dust suppression; radiation dose monitoring; strict hygiene standards, ventilation, and protective clothing; and installation of covers on tailings. Environmental impacts of uranium mine wastes include: excessive radioactivity levels and radon emissions; inappropriate use of tailings and waste rocks; failure of tailings dams; soil, sediment, and ground and surface water contamination; and acid mine drainage.

Further information on uranium mine wastes can be obtained from web sites shown in Table 6.8.

Table 6.8. Web sites covering aspects of uranium mine wastes

Organization	Web address and description
US Environmental Protection Agency (EPA)	*http://www.epa.gov/iaq/radon/* *http://www.epa.gov/radiation/* *http://www.epa.gov/radiation/docs/radwaste/* *http://www.epa.gov/radiation/tenorm/sources.htm* Health effects of radiation and radon exposure; factsheet on uranium mill tailings
US Department of Energy (DOE), Uranium Mill Tailings Remedial Actiont	*http://www.em.doe.gov/bemr96/umtra.htm* *http://www.em.doe.gov/emprimer/erumtra.html* Details on uranium mill tailings remediation programme
US Nuclear Regulatory Commission	*http://www.nrc.gov/reading-rm/doc-collections/fact-sheets/mill-tailings.html* Factsheet on uranium mill tailings
Department of the Environment and Heritage, Supervising Scientist, Australia	*http://www.deh.gov.au/ssd/uranium-mining/index.html* Publications and information on uranium mining in the Alligator Rivers region
Wyoming Mining Association	*http://www.wma-minelife.com/uranium/uranium.html* Uranium mining and milling in Wyoming
Uranium Information Centre	*http://www.uic.com.au* Information on uranium mining and nuclear energy; information sheet on mineral sands
World Nuclear Association	*http://www.world-nuclear.org* Information on nuclear energy and uranium mining
World Information Service on Energy (WISE) – Uranium Project	*http://www.wise-uranium.org* Information on environmental impacts of uranium mining
Radwaste	*http://radwaste.org* Reference source for radioactive waste management