CHAPTER 22

Behavior of Radionuclides
in the Environment

Contents

The main objection against nuclear power is the risk of spread of "radioactivity" (radioactive elements) to the environment where it may cause health effects in humans. We have already discussed such effects (Ch. 18). Here, we are concerned with the chemical aspects of the sources of releases and of the migration of the radionuclides in the environment. Their chemical properties, together with hydrology, determine how fast they will move from their point of entry into the groundwater to water resources used by man; this is schematically illustrated in Figure 22.1. In particular we discuss actinide behavior as these elements have the most hazardous radionuclides which may be released in the different steps of the nuclear fuel cycle, and, especially, from nuclear waste repositories.
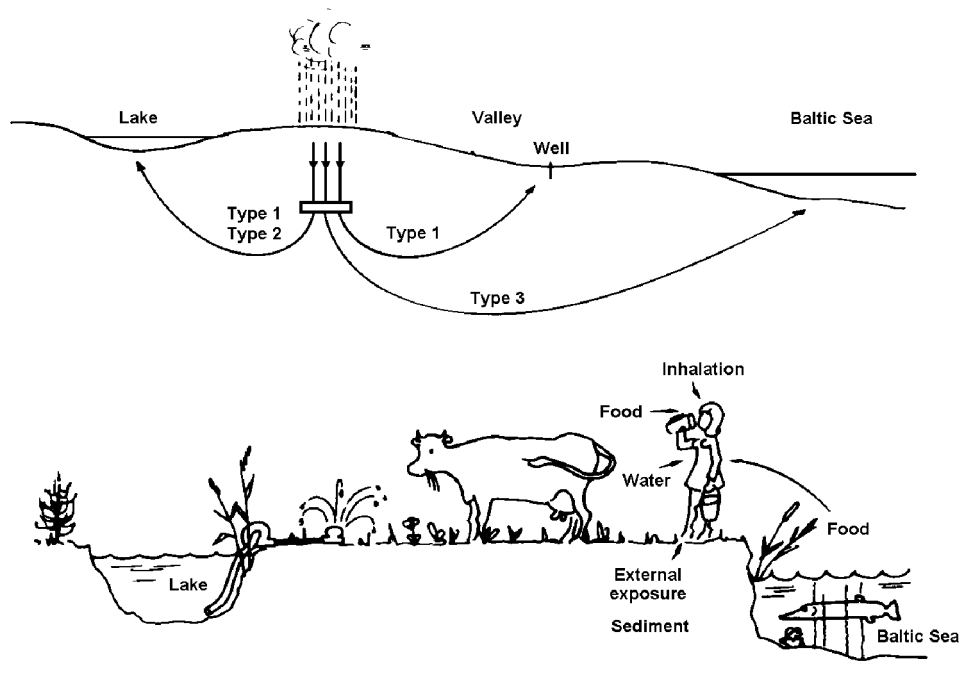
FIG. 22.1. Migration path of radioactive nuclides from a waste repository to man.

22.1. Radioactive releases and possible effects

In earlier chapters, there have been brief discussions of the release of radionuclides to the environment. Such releases occur from mining and milling operations, particularly of uranium ores (§5.5.4), from the nuclear fuel fabrication processes, from normal operation of nuclear reactors (§19.16),from reprocessing of spent nuclear fuel (§21.8), from nuclear weapons production and recovery, from transportation of nuclear material, from testing of nuclear weapons and accidents (§5.10), and from storage of nuclear wastes (which we discuss in subsequent sections). Table 22.1 compares the estimated collective dose to the public from the various activities of the nuclear fuel cycle, from mining and milling through nuclear waste disposal; the significant point is the recognition that the mining operation for uranium is the major contributor in the dose to the global public by quite a large fraction.

An estimate of the total radioactivity, by nuclide, released into the atmosphere by above-ground nuclear tests is given in Table 22.2; the total release is ~ 2 600 EBq. To provide comparison, the estimated global releases from reactors and reprocessing plants are listed in Table 22.3; globally this gives ~ 3.9 EBq from reactors and 3.4 EBq from reprocessing plants up to 1998. The major releases are the noble gases, ^{3}H and ^{14}C. The total ^{14}C release over 30 years is less than one percent of the normal ^{14}C level from cosmic ray

TABLE 22.1. *Collective effective dose to the public from radionuclides released in effluents from the nuclear fuel cycle 1995-97 (UNSCEAR 2000)*

Source	Normalized collective effective dose (manSv/GW$_e$y)
Local and regional effects	
Mining	0.19
Milling	0.008
Mine and mill tailings (releases over 5 years)	0.04
Fuel fabrication	0.003
Reactor operation	
Atmospheric	0.4
Aquatic	0.04
Reprocessing	
Atmospheric	0.04
Aquatic	0.09
Transportation	< 0.1
Solid waste disposal and global effects	
Mine and mill tailings	
Releases of radon over 10 000 y	7.5
Reactor operation	
Low-level waste disposal	0.00005
Intermediate-level waste disposal	0.5
Reprocessing solid waste disposal	0.05
Globally dispersed radionuclides (truncated to 10 000 years)	40

production (Section 5.1.3). Thus, this is a small fraction of the radioactivity released in nuclear weapons testing. To further place the releases in proper relation, an estimate of the total atmospheric release in the Chernobyl accident was 2 EBq (Table 22.4), and in the Three Mile Island Reactor (TMI) accident, 10^{-6} EBq. From such figures the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) estimates that the average annual dose of radiation per person during year 2000 corresponded to:

Natural background	2.4 mSv
Medical diagnostics	0.4 mSv
Nuclear weapons tests	0.005 mSv
Chernobyl accident	0.002 mSv
Nuclear fuel cycle	0.0002 mSv

22.2. Radionuclides of environmental concern

Most of the radionuclides produced in nuclear tests, accidents and in the normal fuel cycle are short lived. In Table 21.3, longer lived fission products and activation products from these systems are listed as these represent the major concern to the general public if they are allowed to enter the environment; we exclude nuclides with insignificant contribution

TABLE 22.2. *Radionuclides released in atmospheric nuclear testing* (UNSCEAR2000)

Radio-nuclide	Half-life	Estimated release Total (EBq)	Radio-nuclide	Half life	Estimated release Total (EBq)
^{3}H	12.33 y	186	^{125}Sb	2.73 y	0.741
^{14}C†	5730. y	0.213	^{131}I	8.02 d	675
^{54}Mn	312.3 d	3.98	^{137}Cs	30.07 y	0.948
^{55}Fe	2.73 y	1.53	^{140}Ba	12.75 d	759
^{89}Sr	50.53 d	117	^{141}Ce	32.50 d	263
^{90}Sr	28.78 y	0.622	^{144}Ce	284.9 d	30.7
^{91}Y	58.51 d	120	^{239}Pu	24110. y	0.00652
^{95}Zr	64.02 d	148	^{240}Pu	6560. y	0.00435
^{103}Ru	39.26 d	247	Pu	14.36 y	0.142
^{106}Ru	1.023 y	12.2			

For the non-gaseous fission products a total non-local fission explosion yield of 160.5 Mt, obtained from measured ^{90}Sr deposition, was assumed in deriving the total amounts released. † For simplicity, all ^{14}C is assumed to be due to fusion.

to the total activity after 10 years. In addition, several heavy radionuclides are formed by neutron capture reactions such as ^{236}U, ^{237}Np, $^{238\text{-}242}$Pu, ^{241}Am, etc.

To assess the potential for these radionuclides to cause harm to humans, their geochemical and biological behavior must be evaluated. For example, since Kr is a chemically inert gaseous element, it would have little effect on a person who inhaled and immediately exhaled the small amount which might be present in the air. By contrast, other nuclides with high activity, ^{90}Sr-^{90}Y and ^{137}Cs-^{137m}Ba, have active geological and biological behavior and can present much more significant radiation concerns to humans. In normal operations, these nuclides would of course be released in quite insignificant amounts, as represented by the value for aquatic releases in reactor operation and reprocessing, Table

TABLE 22.3. *Global release of radionuclides by reactors and reprocessing plants up to 1998* (UNSCEAR2000)

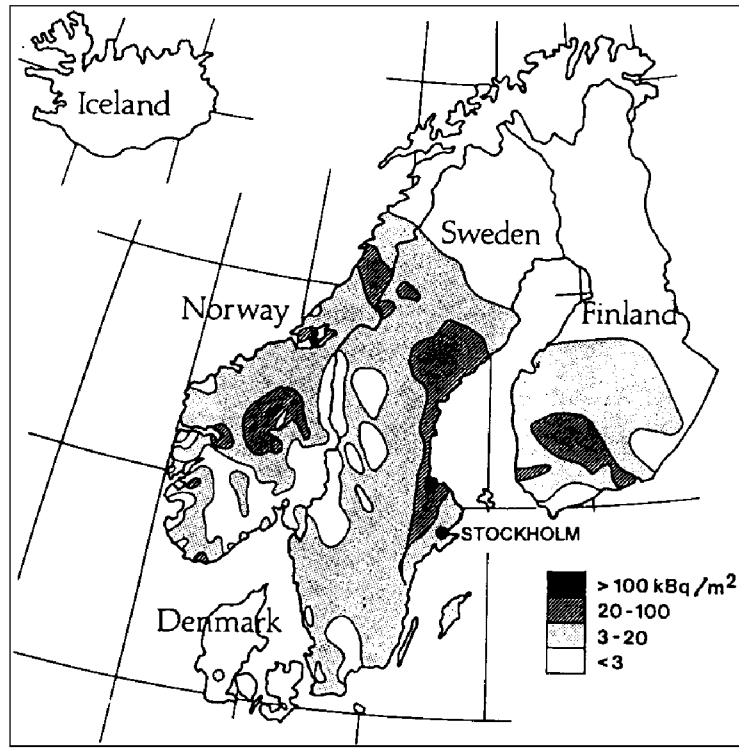| Radionuclides	Reactor releases (PBq)	Reprocessing releases (PBq)
Noble gases	3631	3190
^{3}H	269	144
^{14}C	1.97	0.44
^{90}Sr	–	6.6
^{106}Ru	–	19
^{129}I	–	0.014
^{131}I	0.046	0.004
^{137}Cs	–	40
Particulates	0.121	–
Others	0.839	–
Total	~ 3900	~ 3400

FIG. 22.2. Deposition of ^{137}Cs in Scandinavia from the Chernobyl accident.

19.7 and 21.10. Similarly, the heavy elements (Np, Pu, Am) would not be released in normal operation at levels that would be of concern. We have pointed out that some low level releases as a result of normal operations are allowed by the health authorities, who also monitor these levels. In the effluents from reprocessing plants (e.g. Sellafield in the United Kingdom and La Hague in France), the relatively long-lived nuclides such as ^{3}H, ^{14}C, ^{85}Kr, ^{99}Tc and ^{129}I are of major concern. The liquid effluents from nuclear power plants and from reprocessing plants are about equally responsible for the global collective dose commitment of nuclear power generation (i.e., ~ 0.8 man Sv per GW_ey of the total ~ 2.5 man Sv).

22.3. Releases from the Chernobyl accident

On April 26, 1986, a low power engineering test was being conducted at one of the reactors of the Chernobyl nuclear power station in the Ukraine (then the USSR). The reactor became unstable, resulting in thermal explosions and fires that caused severe damage to the reactor and its building (§§5.10.2 and 20.1.2c). Radioactivity was released over the next ten days until the fires were extinguished and the reactor entombed in concrete. The radioactivity was released as gas and dust particles and initially blown by winds in a northerly direction. Outside Russia, the accident was first detected by increased

TABLE 22.4. *Radionuclides released into the atmosphere in the Chernobyl accident and local contamination*

Nuclide	Half-life	Release tot EBq	%	Core inventory tot EBq	air (Bq m^{-3}) Stockholm [†]	ground (kBq m^{-2}) Gävle area [‡]
^{85}Kr	10.73 y	0.033	≈100	0.033		
^{89}Sr	50.5 d	0.094	4.0	2.4		
^{90}Sr	28.6 y	0.0081	4.0	0.20		
^{95}Zr	64.0 d	0.16	3.2	5.0	0.6	5.9
^{103}Ru	39.4 d	0.14	2.9	4.8	6.4	14.6
^{106}Ru	368 d	0.059	2.9	2.0	1.8	4.0
^{131}I	8.04 d	0.67	20	3.3	15	179
^{133}Xe	5.24 d	1.7	≈100	1.7		
^{134}Cs	2.07 y	0.019	10	0.19	2.4	14.4
^{136}Cs	13.2 d				0.7	6.0
^{137}Cs	30.2 y	0.037	13	0.28	4.5	24.7
^{140}Ba	12.8 d	0.28	5.6	5.0	25.6	2.1
^{141}Ce	32.5 d	0.13	2.3	5.6	0.5	5.9
^{144}Ce	284 d	0.088	2.8	3.1	0.3	3.7
^{239}Np	2.36 d	0.97	3.2	30		2.7
^{238}Pu	87.7 y	3.0×10^{-5}	3	0.001		
^{239}Pu	24100 y	2.6×10^{-5}	3	0.0009		
^{240}Pu	6570 y	3.7×10^{-5}	3	0.0012		
^{241}Pu	14.4 y			0.170		

[†] First days, April 28-29, 1986. [‡] Ullbolsta, outside of Gävle, among highest depositions outside Russia; corrected to April 28, 1986. References: USSR State Comm. on the Utilization of Atomic Energy 1986. The accident at the Chernobyl nuclear power plant and its consequences, IAEA expert meeting 25-29 Aug. 1986, Vienna.

radioactivity levels at the Forsmark nuclear power plant, about 110 km north of Stockholm, Sweden, where it caused a full alarm as the radioactivity was believed to come from the Swedish plant. Subsequently, the radioactivity released at Chernobyl was spread more to the west and southwest (Figure 5.8).

TABLE 22.5 *Nuclide composition of a "hot particle" from Chernobyl compared to reactor fuel after 3 years of burning*

Nuclide	"Hot Particle" (%)	Reactor fuel
^{95}Zr	17.9	17.6
^{95}Nb	20.7	19.3
^{103}Ru	14.2	15.0
^{106}Ru(Rh)	3.5	2.4
^{140}Ba(La)	12.6	11.1
^{141}Ce	15.8	14.3
^{144}Ce(Pr)	15.8	14.4

For the exposed population in the Byelorussia region near Chernobyl the estimated average increased dose in the first year after the accident was approximately the same as the annual background radiation. In northern and eastern Europe in general, the increased exposure during the first year was 25-75% above background levels. The highest dose will be delivered in southeastern Europe and is estimated to be 1.2 mSv up to year 2020, which can be compared to ~ 70 mSv from natural background radiation during the same period. Figure 22.2 shows the levels of ^{137}Cs deposited in Scandinavia in the first days after the accident. Table 22.4 gives the fraction of the core activity released and the air and ground contamination of various nuclides at two Swedish locations.

It was shown that the larger airborne particulates from the Chernobyl accident had a composition which was quite similar to that of the reactor fuel. A comparison of the composition of these "hot particles" with that of the reactor fuel is given in Table 22.5. About a tenth of these hot particles had a high concentration of ^{103}Ru and ^{106}Ru while others were depleted in the ruthenium fission products. The Ru-rich particles may have originated from a part of the reactor where burning graphite produced CO which reduced the ruthenium to non-volatile metallic Ru. In other sections, oxidation occurred, forming volatile RuO_3 and/or RuO_4 which vaporized from the particles.

In contrast to the larger particles, the composition of the smaller ones varied considerably and they were distributed over much greater distances. Other measurements reflect this variability in the fall-out from Chernobyl. For example, 70% of the ^{137}Cs from Chernobyl measured in Great Britain was water soluble. By contrast, the ^{137}Cs measured in Prague, much closer to the accident site, was only 30% water soluble. Further insight into the variety of species present in the Chernobyl dust is found in data on the deposition of some radionuclides during periods of rain, and dry weather. Rainy periods accounted for 70-80% of the total deposition of ^{134}Cs, ^{137}Cs, ^{103}Ru, ^{106}Ru, and ^{132}Te while deposition during dry weather was more important for ^{131}I.

These observations indicate that the speciation of radionuclides in the atmosphere is dependent on their source, their mechanisms of production and the nature of the particular environment. While some species are gaseous, others are associated to particles with properties and suspension times that are strongly dependent on the particle size and density.

22.4. Injection of TRU into the environment

Of the artificial radionuclides released to the environment by nuclear activities, the transuranium (TRU) species are a major concern. This concern arises from the very long half-life of a number of the nuclides as well as their high radiotoxicity values. Although reactor operation and spent fuel reprocessing activities have released small amounts of TRU's to the environment, testing of nuclear weapons has released rather large quantities. Since the first nuclear test detonation in New Mexico in 1945, approximately 3 500 kg of plutonium has been released in atmospheric explosions and another 100 kg in underground tests. This corresponds to about 11 PBq of $^{239+240}$Pu ejected into the atmosphere. In addition 0.6 PBq of ^{238}Pu were released over the south Pacific in the high altitude destruction of the SNAP-9 satellite power source in 1964. By contrast, a total of ~ 0.58 PBq of $^{239+240}$Pu has been released into the Irish Sea from the Sellafield (UK) reprocessing plants between 1971 and 1999; most of this before 1985. About 37 kg of ^{241}Am is present

TABLE 22.6. *TRU released from nuclear tests and from reprocessing (UNSCEAR2000, BNFL and COGEMA)*

Nuclide	Tests (TBq) 1945-1980	Sellafield, (TBq) 1971-84	1985-94	1995-99	LaHague (TBq) 2000
^{237}Np	-	-	0	0.33	
^{239}Pu	6 520				
^{240}Pu	4 350	} 559	} 15	} 0.92	
^{241}Pu	142 000	-	-	21.8	0.039[†]
^{241}Am	-	442	9	0.31	
^{242}Cm	-	-	-	0.052	
$^{243+244}$Cm-	-	-	0.024		

[†] Total α

in the environment from the decay of ^{241}Pu from the nuclear testing. Table 22.6 compares the TRU's released in nuclear tests in the atmosphere, in the Irish Sea from the Sellafield plants, and into the English Channel from the LaHague plants. As the amount of spent nuclear fuel increases, the contribution to the total plutonium in the environment could become more significant over a longer time, especially if nuclear waste disposal sites release actinide elements slowly to the environment. Whatever the sources of plutonium and other actinides, their presence represents a contamination of the environment by highly toxic material. An understanding of the factors involved in their retention and/or migration in the ecosphere is therefore highly desirable. Studies of the environmental behavior of releases from tests provide data needed to understand and predict the behavior of smaller releases from the nuclear power industry. Therefore, in the next few paragraphs we concentrate our discussion to the behavior of the actinide elements in the environment, particulary the mobility of plutonium.

The majority of the plutonium from weapons testing was injected initially into the stratosphere. The plutonium originally in the weapon which survived the explosion would have been formed into high-fired oxide which would be expected to remain insoluble as it returned to earth. Such insoluble particles would have sunk in a rather short time into the bottom sediments of lakes, rivers, and oceans or would become incorporated in soils below the surface layer. However, in most nuclear weapon explosions a considerable amount of plutonium is generated in the explosion via ^{238}U (n,γ) reactions and subsequent α-decay of the product ^{239}U, ^{240}U, ^{241}U, etc. In total, about two thirds of the plutonium released was generated in this way. The nuclides from the (n,γ) reactions would exist as single atoms, and, hence, were never formed into high-fired oxides. The plutonium from this formation path would have been soluble and, as a result, more reactive and its behavior would be more similar to that of plutonium released from nuclear reactors, reprocessing plants and from nuclear waste repository sites.

22.5. Present levels of TRU in the ecosphere

The United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), in 2000 reports data that corresponds to the following total average global

TABLE 22.7. *Concentration of plutonium in filtered samples of natural waters*

Water	Concentration of Pu (M)
Lake Michigan	2.0×10^{-17}
Great Slave Lake, Canada	1.5×10^{-17}
Okefenokee River, Florida	1.5×10^{-16}
Hudson River, New York	1.0×10^{-17}
Irish Sea:	
1 km from Windscale	1.6×10^{-14}
110 km from Windscale	1.1×10^{-15}
Mediterranean	2.6×10^{-18}
North Pacific (surface)	3.0×10^{-17}
South Pacific (surface)	1.0×10^{-17}

Samples were passed through 0.45 μm filters.

nuclide depositions from atmospheric nuclear weapon tests: [89]Sr 11, [90]Sr 1.2, [95]Zr 19, [106]Ru 12, [137]Cs 1.8, [239]Pu 0.013, [240]Pu 0.009, and [241]Pu 0.278 kBq m^{-2}. Some of these radionuclides have now decayed because of their short half-lives and the end of atmospheric testing in 1980 and almost all of the [241]Pu has decayed to [241]Am.

Near test sites, reprocessing facilities, etc., the concentration of plutonium in the soil and water is much higher than in more distant locations. Generally, the great majority of plutonium is associated with sub-surface soils or sediments or with suspended particulates in water. For example, when vegetation, animals, litter and soils are compared, ≥99% of the plutonium is present in the soil. Similarly, in shallow bodies of water, more than 96% of the plutonium is found associated with the sediments. However, it is via the species that are soluble or attached to suspended colloids and/or particulate matter in water that plutonium is transported in the environment. Analysis of vertical plutonium migration in soils near Chernobyl and in eastern Europe from the Chernobyl accident has shown that most of the plutonium is still in the first 0.5 cm from the surface for soils with significant humic acid content. In these soils, the plutonium is mostly associated with the insoluble calcium-humate fraction. In non-humic, carbonate rich soils, the plutonium has moved several centimeters downward. Migration rates of ≤0.1 cm y^{-1} is associated with the humic soils and of 1-10 cm y^{-1} with the carbonate rich ones. Presumably, migration is retarded by the interaction with the immobilized humic material in soils.

In subsurface oxic soil near Los Alamos National Laboratory, USA, plutonium is relatively mobile and has been transported primarily by colloids in the 25-450 μm size range. Moreover, the association with these colloids is strong and removal of Pu from them is very slow. By contrast, near Sellafield in wet anoxic soil, most of the Pu is quickly immobilized in the sediments although a small fraction remain mobile. Differences in oxidation state (Pu(V) vs. Pu(IV)) as well as in humic content of the soils may explain these differences in mobility.

Table 22.7 lists the concentration of plutonium, after filtration (0.45 μm), in the surface layers of some natural waters. The higher concentration in the Okefenokee River is assumed to reflect the effect of complexing by humic materials. This agrees with the observation that

adding humic material to seawater samples containing plutonium increases the solubility by more than a factor of five over a period of one month.

It is difficult to obtain reliable values of plutonium concentration in natural aquatic systems as it is very low, approximately 0.001 dpm per liter sea water. Moreover, the plutonium associated with suspended particles may be more than an order of magnitude greater than that in true solution. In tests of water from the Mediterranean Sea, filtration (0.45 μm) reduced the concentration of plutonium by a factor of 25. In laboratory tests with filtered seawater to which plutonium was added, after one month the total concentration of Pu was 1.3×10^{-11} M, but only 40% (5×10^{-12} M) was in solution as ionic species and the other 60% was probably in colloidal form. The mean residence time of Pu in the water column is proportional to the concentration of particulate matter. As a consequence, > 90% of the Pu is rapidly removed from coastal waters whereas, in mid-ocean waters where the particulate concentrations are lower, the residence time for Pu is much longer.

22.6. Actinide chemistry in the ecosphere

22.6.1. *Redox properties*

Before proceeding to more detailed discussion of the behavior of actinides in the environment, it is useful to review some of their chemical properties. A general discussion of the actinide solution chemistry is given in §16.3; here, the focus is on their behavior in aqueous solutions and primarily in solutions of pH 5 - 9 which is the pH range of natural waters (e.g. the oceans have pH = 8.2). The actinide ions have an unusually broad range of oxidation states in aqueous solution, from II to VII; The II and VII States are not discussed further as they do not form in ecosystems. Following the normal pattern for polyvalent cations, lower oxidation states are stabilized by more acidic conditions while higher oxidation states are more stable in basic solutions. Of course, this generalization can be negated by other factors, such as complexing, which may cause a reversal of the relative stability of different oxidation states. The greater strength of complexing of An(IV) cations relative to that of An(III) can significantly increase the apparent redox stability of the An(IV) species compared to An(III). The greater tendency to hydrolysis of Pu(IV) causes Pu(III), which is stable in acid solution, to be oxidized to Pu(IV) in neutral media. The disproportionation of Pu(V) is discussed in Chapter 16 where it is pointed out that in the

TABLE 22.8. *Plutonium oxidation states (in % of total Pu) in natural waters*

State	Pu(III+ IV)	Pu(V)	Pu(VI)
Rain	34	66	
Mediterranean	42	58	
Irish Sea	23	77	0
Pacific (I)	39	52	9
Pacific (II)	40	46	14
Lake Michigan	13	87	0

$$U(III) \xrightarrow{-0.631\ V} U(IV) \xrightarrow{+0.613\ V} U(V) \xrightarrow{+0.063\ V} U(VI)$$

- U(III)→U(IV): −1.95±0.17 ; −2.78±0.35
- U(IV)→U(V): +0.08±0.12 ; −0.03±0.24
- U(V)→U(VI): −0.23±0.05 ; −0.69±0.24
- U(IV)→U(VI): +0.338 V ; −0.07±0.08 ; −0.36±0.12

$$Np(III) \xrightarrow{+0.155\ V} Np(IV) \xrightarrow{+0.739\ V} Np(V) \xrightarrow{+1.136\ V} Np(VI)$$

- Np(III)→Np(IV): −1.13±0.14 ; −1.88±0.24
- Np(IV)→Np(V): +0.15±0.13 ; −0.09±0.24
- Np(V)→Np(VI): +0.81±0.08 ; +0.38±0.24
- Np(IV)→Np(VI): 0.938 V ; +0.48±0.09 ; +0.15±0.12

$$Pu(III) \xrightarrow{+0.982\ V} Pu(IV) \xrightarrow{+1.170\ V} Pu(V) \xrightarrow{+0.916\ V} Pu(VI)$$

- Pu(III)→Pu(IV): −0.39±0,15 ; −1,04±0.24
- Pu(IV)→Pu(V): +0.70±0.12 ; +0.52±0.24
- Pu(V)→Pu(VI): +0.60±0.04 ; +0.16±0.24
- Pu(IV)→Pu(VI): +1.043 V ; +0.65±0.08 ; +0.34±0.12

FIG. 22.3. Redox potential diagrams of U, Np and Pu; the reduction potentials as listed are for pH values: pH= 0; pH= 8; pH= 14.

higher pH and very low concentrations of Pu in natural waters, disproportionation is not a factor in the redox behavior of plutonium.

The actinide elements in a particular oxidation state (e.g. Th(IV), U(IV), Pu(IV), Np(IV), Am(IV)) have similar behavior. However, their redox behavior is quite different, as mentioned in Chapter 16. The pH affects this redox behavior significantly as reflected in Figure 22.3 which compares the redox potentials of U, Np and Pu at pH = 0, 8 and 14.

Am (III) is the most stable oxidation state in aqueous solutions while Pu(III) and Np(III) are present under reducing conditions (e.g. anoxic waters). Th(IV) is the common and stable state for that element. U(IV) and Np(IV) do not react with water but are oxidized by O_2 in oxic systems. Pu(IV) is stable at low concentrations in acidic solution, but $Pu(OH)_4$ has a very low solubility product.

NpO_2^+ is stable except at high acidities and high concentrations under which conditions it disproportionates. UO_2^+ and PuO_2^+ increase in stability as the pH is increased. U, Np and Pu form AnO_2^{2+} ions in solution with the stability decreasing in the order U > Pu > Np. UO_2^{2+} is the most stable uranium species in natural waters.

Redox reactions can be induced in the actinide ions by secondary effects which can be significant in natural waters. In the presence of higher levels of radiation (e.g. α-emission from the actinides or β,γ from fission products), the radiolytic products, such as the free radicals, peroxide, etc., would also induce redox changes.
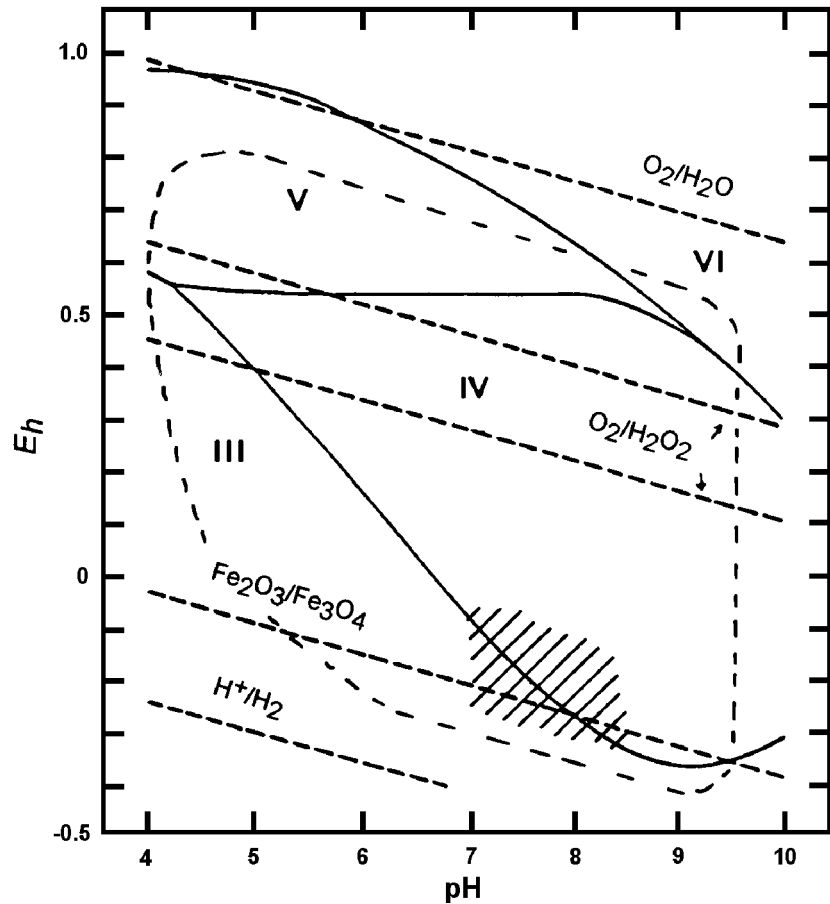
FIG. 22.4. Eh-pH (Pourbaix) diagram showing stability areas for Pu(III), Pu(IV), Pu(V) and Pu(VI); at the division line there is an equal concentration of the two oxidation states.

Redox properties are often described by the aid of *potential-pH* (or *Pourbaix*) diagrams, Figure 22.4. The shaded area represents typical groundwaters in granitic rock, containing iron minerals; such waters are usually reducing, i.e. have Eh-values below 0. Natural groundwaters (including oceans, lakes, rivers, etc) fall within the area enclosed by the dashed curve; they can have rather high Eh values due to atmospheric oxygen, and also be rather alkaline in contact with carbonate rocks. The sloping lines follow the Nernst equation (defined by eqn. (9.4)). We discuss this Figure further in §22.7.1.

22.6.2. *Hydrolysis*

Hydrolysis is an important factor in actinide behavior in natural waters as the pH is high enough to result in such reactions as:
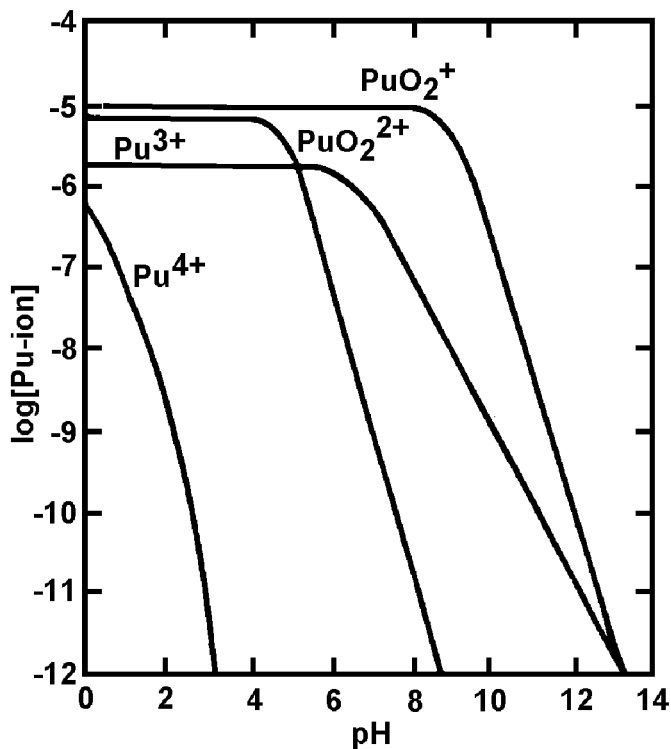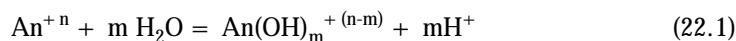
FIG. 22.5. Concentration of free plutonium ions at different oxidation states in solutions of different pH, showing the effect of hydrolysis.
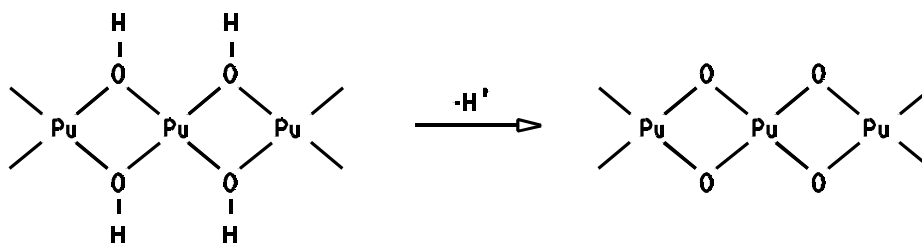
$$An^{+n} + m\ H_2O = An(OH)_m^{+\ (n-m)} + mH^+ \qquad (22.1)$$

The order of increasing pH for onset of hydrolysis follows the sequence:

$$An^{4+} > AnO_2^{2+} > An^{3+} > AnO_2^{+} \qquad (22.2)$$

The variation of the concentration of the free (non- hydrolyzed) cations with pH is shown for the oxidation states of III to VI of Pu in Figure 22.5. These curves are based on estimated values of the hydrolysis constants, but are of sufficient accuracy to indicate the pH values at which hydrolysis becomes significant (e.g. $\sim$ 6-8 for Pu^{3+}, ≤ 0 for Pu^{4+}, 9-10 for PuO_2^{+} and 4-5 for PuO_2^{2+}.

The study of plutonium hydrolysis is complicated by the formation of oligomers and polymers once the simple mononuclear hydrolytic species start forming. The relative mono/oligomer concentrations are dependent on the plutonium concentration: e.g. the ratio of Pu present as $(PuO_2)_2(OH)_2^{2+}$ to that as $PuO_2(OH)^{+}$ is 200 for *total* $[Pu]_T$ 0.1 M, decreases to 5.6 for 10^{-4} M and is only 0.05 for 10^{-8} M. The hydrolysis of Pu^{4+} can result in the formation of polymers which are very difficult to convert back to simpler species. Generally, such polymerization requires $[Pu]_T > 10^{-6}$ M. However, the irreversibility of polymer formation prevents the destruction of the polymers by dilution of more con-

centrated hydrolysed solutions to concentrations below 10^{-6} M. Soon after formation, such polymers in solution can be decomposed to simpler species by acidification or by oxidation to Pu(VI). However, as the polymers age, the depolymerization process requires an increasingly vigorous treatment. A reasonable model of the aging involves initial formation of aggregates with hydroxo bridging with conversion over time to structures with oxygen bridging:

The relative percentage of oxygen bridges presumably determines the relative inertness of the polymers. The polymers apparently increase in aggregate size as the pH increases. At pH 4, the polymers are small enough that essentially all of the Pu remains suspended in solution after a week while at pH 5 less than 10% remains in solution and at pH 6, only 0.1% remains.

22.6.3. *Solubilities*

In marine and natural waters, the limiting solubility is usually associated with either the carbonate or the hydroxide depending on the oxidation state, pH and carbonate concentration. For example for Am^{3+}, the reported value of the solubility product ($\log K_{s0}$, eqn. 9.21) is -26.6 for crystalline $Am(OH)_3(c)$ at very low ionic strength and -22.6 for $Am(OH)(CO_3)(c)$. At pH 6, if $[CO_3^{2-}]_{free} > 10^{-12}$ M and at pH 8, if $[CO_3^{2-}]_{free} > 10^{-8}$ M , the solubility of Am^{+3} would be expected to be limited by the formation of $Am(OH)(CO_3)$.

Plutonium solubility in marine and natural waters is limited by the formation of $Pu(OH)_4(am)$ (for amorphous) or $PuO_2(c)$ (for crystalline). The K_{s0} of these species is difficult to measure, in part due to the problems of the polymer formation. A measured value for $Pu(OH)_4(am)$ is $\log K_{s0} = -56$. This value puts a limit on the amount of plutonium present, even if Pu(V) or Pu(IV) are the more stable states in the solution phase. Moreover, hydrolyzed Pu(IV) sorbs on colloidal and suspended material, both inorganic and biological.

The strong preference for neptunium to form the NpO_2^+, which has relatively weak complexing and hydrolysis tendency, lead to solubilities as large as 10^{-4} M under many geochemical conditions. However, the reducing environment found at large depths in some granites would make Np(IV) the dominant oxidation state. As with plutonium, the solubility of neptunium in all oxidation states seems to be limited by the low solubility of $Np(OH)_4$ (am) or $NpO_2(c)$.

In oxic waters, uranium is present as U(VI) and strongly complexes with carbonate; e.g. in sea water, the uranium is present at 10^{-8} M concentration as $UO_2(CO_3)_3^{4-}$. The solubility of uranium in some waters may be limited by the formation of an uranyl silicate species.

22.7. Speciation calculations

An essential step in the safety analysis of potential waste repositories is the prediction of what chemical species are formed in the actual water. For example, the relatively high solubility of uranium in sea water is due to this strong carbonate complexation which forms $UO_2(CO_3)_3^{4+}$. Figure 22.6 shows the variation of uranyl species in a surface water under normal atmospheric pressure of CO_2 ($p_{CO2} \sim 3.2 \times 10^{-4}$; $\log[CO_3^{2-}] = 2pH - 18.1 + \log p_{CO_2}$). These speciation diagrams are calculated from the equilibrium constant for formation of each species plus mass balance equations. In this section we describe the use of equilibrium constants in modeling the speciation in a natural water.

Assume the reactions $M + nX = MX_n$ where X is OH^-, and CO_3^{2-} and $n = 1$ to 3. The equilibrium constants, expressed as β are given by (cf. eqn. 9.22):

$$\beta_n = [MX_n]/[M] [X]^n \qquad (22.3)$$

The equilibrium constants for Am(III) are listed in Table 22.9 for hydrolysis and CO_3^{2-} complexation. Let us consider the case of Am(III) should it be released into the environment.

The first step in modeling the speciation of Am(III) is to rearrange the above equation to express the ratio of complexed to free metal, e.g. (omitting ionic charges)

$$[AmX]/[Am] = \beta_1 [X] \qquad (22.4)$$

$$[AmX_2]/[Am] = \beta_2 [X]^2 \qquad (22.5)$$

and so forth. The mass balance equation is:

$$[Am]_T = [Am] + [AmX] + [AmX_2] + \dots \qquad (22.6)$$

where $[Am]_T$ is the total analytical concentration of americium. Dividing by $[Am]$ gives:

$$[Am]_T/[Am] = [Am]/[Am] + [AmX]/[Am] + [AmX_2]/[Am] + \dots \qquad (22.7)$$

TABLE 22.9. *Equilibrium Constants for Am(III)*

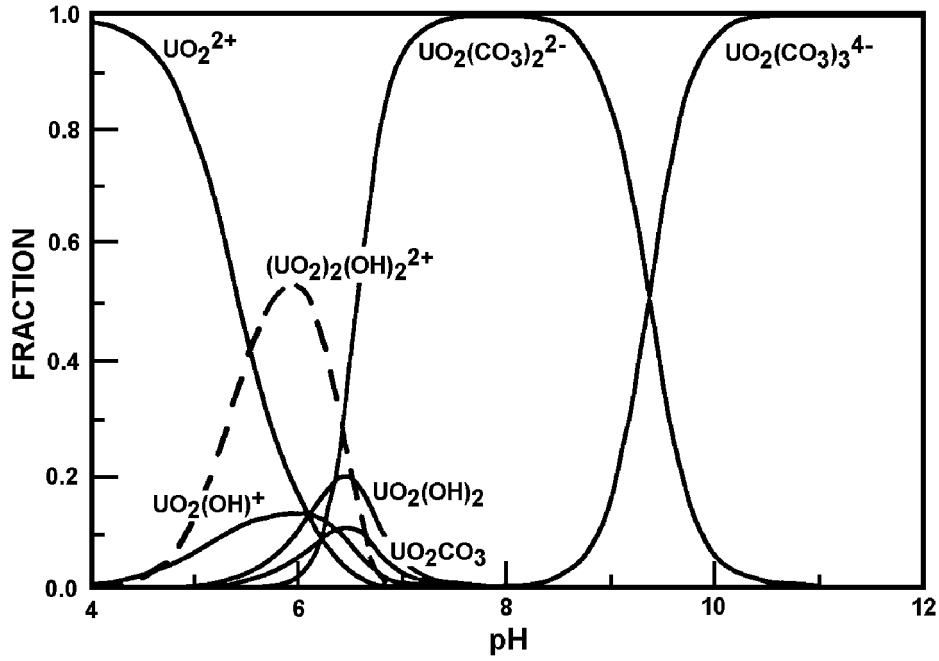| Species	$\log\beta_n$	Species	$\log\beta_n$
$Am(OH)^{2+}$	6.44	$Am(CO_3)^+$	5.08
$Am(OH)_2^+$	13.80	$Am(CO_3)_2^-$	9.27
$Am(OH)_3$	17.86	$Am(CO_3)_3^{3-}$	12.12

FIG. 22.6. Fraction of uranium species in water with natural carbon dioxide content and at different pH, showing hydrolysis and CO_3^{2-} complexation.
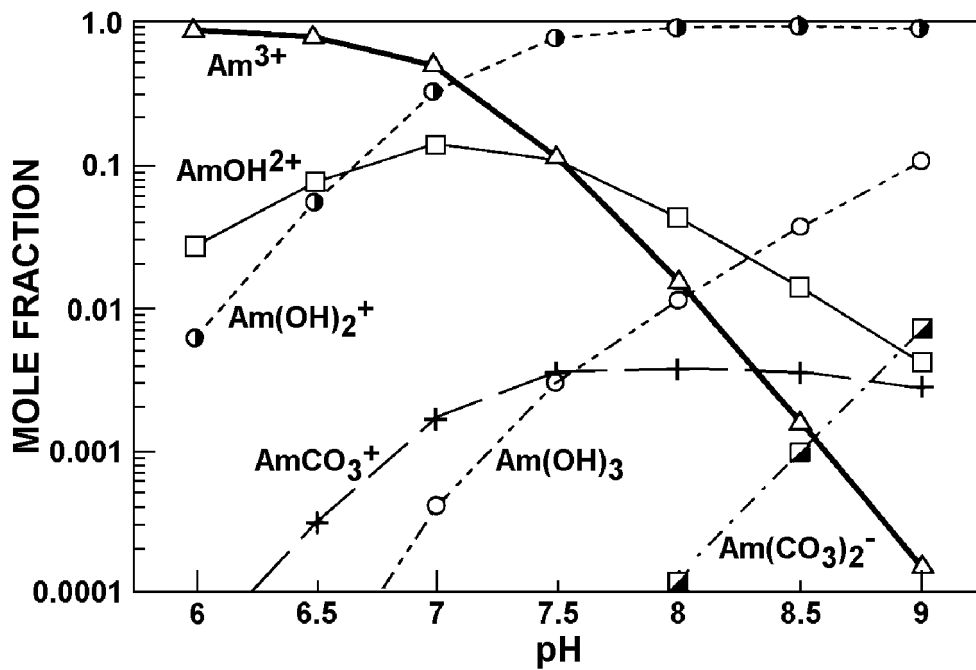

FIG. 22.7. Results of speciation calculations for Am(III) in natural water.
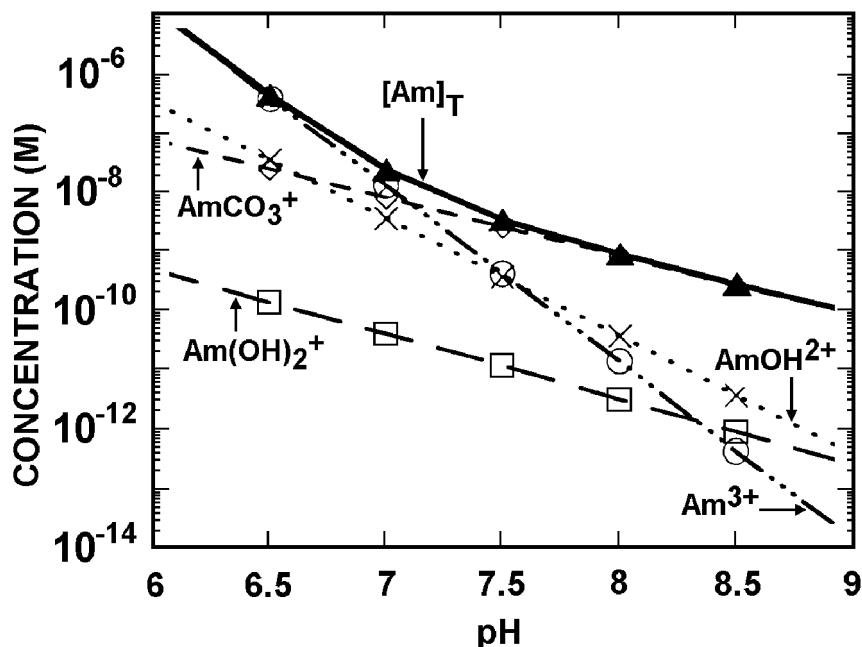
FIG. 22.8. Results of speciation calculations for Am(III) in natural water, taking into account the low solubility of Am(OH)$_3$.

$$[Am]_T/[Am] \ = \ 1 \ + \ \beta_1 \ [X] \ + \ \beta_2 \ [X]^2 \ + \ ... \qquad (22.8)$$

and

$$\alpha_n = \ \beta_n \ [X]^n \ ([Am]/[Am]_T) \qquad (22.9)$$

where α_n is the fraction of all americium in the form of AmX$_n$. With these equations, β_n's, and a given value of $[Am]_T$, we can calculate the concentration of each species for any value of $[X]$. In Figure 22.7 the speciation of Am(III) as hydroxide and carbonate complexes is shown as a function of pH. The concentration of CO_3^{2-} is based on the atmospheric partial pressure (3.2×10^{-4} atm) and the resultant concentration of CO_3^{2-} at different pH values in a natural water.

  If the solubility is limited by a solid phase for which the K_{s0} is known, the actual value to be expected for each species can be calculated by assuming no over-saturation. These can be included in the mass balance equation to predict the total minimum solubility. If log K_{s0} = - 28.9 is assumed for Am(OH)$_3$, Figure 22.8 shows the results of such a calculation for the solubility of americium in the same system as in Figure 22.7, but now including the effect of the limited solubility of Am(OH)$_3$.

  We have stated that Pu(V), as PuO$_2^+$, is the dominant dissolved species while Pu(OH)$_4$ is the solubility limiting precipitate. The redox reaction can be written as:

$$PuO_2^+ \ + \ 4 \ H^+ \ + \ e^- \ = \ Pu^{4+} \ + \ 2 \ H_2O \qquad (22.10)$$
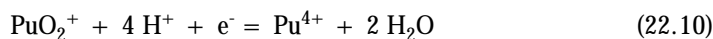
The E° value for the IV/V pair is 1.17 V. Using the equilibrium expression with the Nernst equation, assuming the redox potential in a fresh water lake to be 0.4 V, we obtain at pH 7:

$$[PuO_2^+]/[Pu^{4+}] \approx 10^{15}$$

From the value of log K_{s0} = -56 for $Pu(OH)_4$(am) we can calculate that $[Pu^{4+}]$ in a solution of pH = 7 in contact with solid $Pu(OH)_4$ is 10^{-28} M. This gives us a value of $10^{15} \times 10^{-28} \approx 10^{-13}$ M for the expected concentration of PuO_2^+ in this solution.

A number of geochemical modeling codes have been developed which use such speciation and solubility equilibrium equations to calculate the concentration of different species of a metal ion as well as its net solubility in various waters (common codes are PHREEQE and EQ 3/6). The results from such calculations are as good as the equilibrium constants or the thermodynamic values used in the calculations. Also, most important, the calculations must include the equilibrium equations for *all species in solution* which contribute significantly to the solution phase concentrations and *all solids* which can provide the limiting solubility to the solution species. Furthermore, the *degree of oversaturation* with regard to each solid phase must be prescribed in order to calculate a realistic speciation. These modeling codes are presently based on the assumption that the natural systems are all at equilibrium whereas in nature this may not be true. Many systems are kinetically controlled and are often in a steady state, but not in true equilibrium. In these cases, perhaps the majority of the systems, the equilibrium modelling codes cannot accurately describe the actual conditions, but may provide a set of limiting species, approximate relative concentrations and baseline net solubilities. A further complication arises in assessing the role of colloids, and of sorption which may reduce the concentration of soluble species below that estimated for the least soluble solid phase. On the other hand, sorption on suspended colloids may also increase the total concentration (dissolved plus amount in colloids, e.g. Pu in sea water §22.5). In general, the equilibrium code calculations can easily give lower limit values of maximum solubilities by assuming no oversaturation. Such calculations are valuable in waste management risk assessment since, if the lower limit solubilities from the equilibrium calculations fall well below the accepted safety limits even when assuming reasonable degrees of oversaturation, it is very likely that the actual total concentrations will also be below the acceptable limits, cf. Fig.22.10, Table 22.10 and §22.10.

22.7.1. *Calculated species in solution*

The diversity of reactions which actinides can undergo in natural waters is presented schematically in Figure 22.9. Complexation by anions such as hydroxide, carbonate, phosphate, humates, etc. determine the species in solution. Sorption to colloids and suspended material increases the actinide concentration in the water while precipitation of hydroxides, phosphates, carbonates, and/or sorption to mineral and biological material limit the amount in the solution phase.

In natural oxic waters, americium is present in the trivalent and thorium in the tetravalent state while uranium is hexavalent, UO_2^{2+}. The total concentrations of uranium and thorium in surface sea water are 1.1-1.5×10^{-8} and $\sim 2.5 \times 10^{-12}$ M, respectively in both the Atlantic
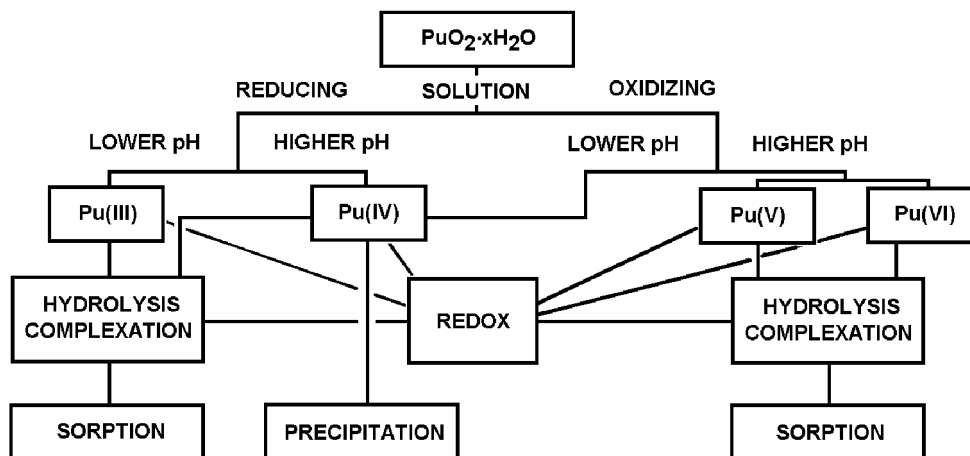
FIG. 22.9. Speciation diagram for the range of reactions to be considered in studying the environmental behavior of plutonium.

and Pacific oceans. The amount of uranium associated with particulate matter in the water is small. By contrast, for tetravalent ^{232}Th (originating from thorium minerals), about 50% is bound in aluminosilicate particles and 50% is dissolved (e.g. passes through a 1 μm filter). For ^{228}Th and ^{230}Th (radiogenic decay products), about 90% is found in solution. Sorption of ^{234}Th tracer is a reversible process, possibly due to an organic material coating on the surface with increased sorption as the particles age. In such studies, solubility is defined as passage through a 0.45 μm filter. Speciation calculations show typically that thorium occurs as a hydrolyzed species whereas uranium is present in surface waters normally as the $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ species. In neutral waters of very low carbonate content, speciation calculations indicate that uranyl cations hydrolyze to form oligomers for total uranyl concentrations as low as 10^{-7} M.

Neptunium, in oxic waters, is present in the pentavalent state. The hydrated cation is calculated to be the dominant species for pH$\leq$8 unless the free carbonate concentration exceeds approximately 10^{-4} M in which case $NpO_2(CO_3)_n^{1-2n}$ is more common.

The rather similar values for the plutonium reduction half reactions at pH 8 indicate that plutonium may exist in oxic waters in more than one oxidation state. The reduction potential at pH 8 of the Pu(III)/Pu(IV) couple indicates that Pu(III) is unlikely to exist in oxic waters in the absence of a reductant, but may be present in anoxic waters. Each oxidation state of plutonium differs in chemical behavior from that of the other states so modelling the geochemical behavior of plutonium must include the correct oxidation state, or states, of plutonium which are likely to be present in a particular system.

In principle, the calculation of the oxidation states of plutonium requires knowledge of the redox potential, Eh, of the aqueous phase. However, the Eh measured with a certain type of electrode may not be the potential for the particular redox couple with which the plutonium reacts. One of the reasons for this is that the Eh-electrode usually catalyses the reaction rate for its specific redox couple. For example, in surface sea water, the measured Eh is about 0.8 V and is due to the O_2/H_2O couple. In the log Eh versus pH diagram,

Figure 22.4, the area of existence of plutonium in different oxidation states, including the effects of hydrolysis and carbonate complexation, is marked by roman numerals. From that diagram, it can be seen that Pu(VI) would be the predominant state in solution in the ocean. In fact, the predominant species is Pu(V). Table 22.8 summarizes the reported oxidation state distribution in several natural systems.

Like NpO_2^+, PuO_2^+ has a low tendency to hydrolysis and complexation and is much less likely to be sorbed to solid surfaces and on colloidal particles than the Pu species in other oxidation states. As a consequence, plutonium can be expected to migrate most rapidly if it is in the pentavalent oxidation state. The total solubility is limited by the formation of the highly insoluble $Pu(OH)_4$. The sorption of hydrolyzed Pu(IV) in neutral water on mineral and organic-coated surfaces is accountable for the very low concentrations of dissolved Pu even in the absence of $Pu(OH)_4$(am) or PuO_2(c). Desorption is accomplished only by strong complexing and/or redox reagents. For example, citrate extracts little plutonium from soil, but a combination of citrate and the redox agent dithionite provides good extraction. The intractable nature of $Pu(OH)_4$ and its strong tendency to sorb on surfaces is a dominant and often controlling feature of plutonium geochemistry.

Silicates and humic substances present in natural waters form colloids and pseudocolloids with which actinides can react. The pseudocolloids formed by humic substances in ground waters have been shown to be efficient scavengers of americium and plutonium.

22.8. Natural analogues

The geochemical modeling calculations based on measured equilibrium data are of primary importance in the safety assessments of proposed nuclear waste repositories (and should be important for other waste repositories as well). Another useful tool in such assessments is the data from studies of natural analogue sites.

The modeling calculations use data from laboratory and field studies which have been obtained over the last few decades. These data are used in the codes to predict the solubilities, and nuclide migration of material which might be released from nuclear repositories over thousands and, even, hundreds of thousands of years. It is not possible to demonstrate rigorously that the models used are accurate as they may simplify the natural system, use incorrect data or misrepresent (possibly, ignore) important processes which occur over very long time periods. However, some validation of the models and data used in the modeling calculations can be obtained from careful comparison of calculated values with those measured at appropriate geologic sites, known as a *natural analogues.*

The natural analogue sites are areas in which uranium ores have been present for geologic time periods. In most cases, these sites have not been affected by human activities, so the record of geologic, long term effects are well preserved. A number of such sites are being studied around the world; studies from a few sites of different characteristics are reviewed here.

From studies of granitic sites, the dominant role of fractures and fissures in the transport of fluids has been convincingly demonstrated. Thus any model of water in a granitic site must include both advection which is dominant in the fractures and fissures, and diffusion which is important in regions of highly altered rocks ("alteration rims"). In clays, mass

transport seems to proceed primarily by ionic and molecular diffusion although some fluid mass transport occurs at discontinuities in the formation.

Often, the mobilization of many elements (e.g. U, but not Th, in crystalline rocks) is correlated with the flow of oxidizing water. The mobilization and fixation of uranium involves complexation, redox and retention on minerals via adsorption, and ion exchange. In clay media, the redox potential is strongly buffered if significant amounts of organic substances are present.

In a section of the Pocos de Caldas (Brazil) formation, most of the thorium and the rare earths, and, to a lesser extent, the uranium, is associated with goethite (FeOOH) particles and transport by organic colloids is much less important. This region is reducing, as shown by the presence of Fe(II). However, in another region of this formation, the thorium and rare earths have a much higher mobility and are associated with organic (humic) colloids. At an analogue site in Scotland, the flow from the ore has passed into a peat bog in which the uranium is associated predominantly with humic material while the Th is found on Fe/Al oxyhydroxide colloids and particles. In many clay deposits, the organic material is most significant in maintaining a reducing potential which restricts actinide migration and provides a sorption source of the mobilized fraction.

22.9. The Oklo reactor

Analysis of the Oklo natural reactors (§19.10) indicates that they must have lasted for 100 000 to 500 000 years with criticality occurring periodically. They probably would have consumed about twelve metric tons of ^{235}U, releasing a total energy of 2 – 3 GWy at a probable power level of ~ 10 kW. About 1.0 – 1.5 t of ^{239}Pu were formed by neutron capture in ^{238}U, but the half-life of ^{239}Pu has resulted in its total decay to ^{235}U. Since a few samples enriched in ^{235}U (presumably due to this decay) have been found, it is believed that in some places in Oklo breeding conditions may have temporarily existed. The decaying fission products are estimated to have had 10^{28} β, γ disintegrations over the operating time of the reactors. The average energy release in the reactor zone was ~ 50 W m^{-2} which is several times greater than that planned for geological nuclear waste repositories. As a consequence, it is estimated that the fluids in the inclusions of the mineral grains in the Oklo reactors had temperatures of 450 to 600°C, well above those anticipated in deep waste repositories. There is evidence of connectively driven circulation of the fluids for distances of 30 m from the main reactor zones as well as significant dissolution and modification of minerals due to the thermal and radiation conditions. Redistribution of some elements resulted from the convective flow of the hot liquids.

The uranium minerals appear to have remained relatively stable despite this heating process. The uranium and the lanthanide elements show evidence of some small degree of localized redistribution, but were mostly retained within the reactor zone. By contrast, fission product rare gases, halogens, molybdenum and the alkali and alkaline earth elements migrated significant distances from the reactor zones. In general, it seems that elemental redistribution took place over a period of 0.5 to million years while the area was thermally hot (during and after nuclear criticality). It has been estimated that as much as a total of 10^{12} liter of hot water flowed through the reactor zones. The water leaving the reactor zones had 5×10^{-3} g U m^{-3} and ~ 10^{-10} M concentrations of Tc, Ru, and Nd. The Tc and

Ru were oxidized to TcO_4^- and RuO_4^-, and these soluble oxyanions moved with the water as it flowed from the area, creating significant (25 – 35%) deficiencies of these elements in the reactor zones. The Nd was less soluble and, apparently, migrated much less during this hot period. For Tc and Ru, the migration rate seems to have been ~ 10^{-5} m y^{-1} in water moving at a flow of 5 m y^{-1}.

A very important observation is the evidence in Oklo that the plutonium produced by the reactors did not move during its lifetime from the site of its formation.

In summary, essentially 100% of the Pu, 85 – 100% of the Nd, 75 – 90% of the Ru and 60 – 85% of the Tc were retained within the reactor zones. The migrating fission products were held within a few tens of meters of these zones. Thermodynamic calculations of the temperature dependent solubilities indicate that the loss of fissiogenic elements is diffusion controlled, whereas, retention in the surrounding rocks is due to temperature dependent deposition from an aqueous solution.

While the conditions at Oklo differ in a number of aspects from those expected in nuclear repository sites, they frequently were much less favorable to retention of the radionuclides. The lack of migration of the actinides and the much slower release of Tc agree with the predictions of laboratory studies and indicate their value in validating the safety of nuclear repositories.

22.10. Performance assessments of waste repositories

In this Chapter we have presented some information on studies of the environmental behavior of some fission products and actinides. We have shown how laboratory data can be used in speciation calculations to predict solubilities, etc. The knowledge gained from studies of natural analog sites and, very importantly, from the Oklo natural reactor site, has been reviewed. All of these types of studies and data are of use in assessing the probable ability of nuclear waste repositories to protect the public over the millennia required for the radioactivity to decay. The most common design goal for these repositories is that no radioactivity shall be released within the next 1 000 years, and that the leakage after that time would be so small that it presents no danger to living species. The Environmental Protection Agency (EPA), USA, standard requires that no more than 1 000 cancers shall be caused in 10 000 years by radionuclides released from the waste, using the ICRP predictions of radiation dose effects (Ch. 18).

The initiated radioactive inventory for spent reactor fuel consists of actinides, fission products and activation products. As noted previously, (Ch. 21) the shorter lived fission products, such as ^{90}Sr and ^{137}Cs, and transuranic elements, such as ^{238}Pu, ^{241}Pu, ^{244}Cm, are the main contributors to the radioactivity. However, performance assessments strongly indicate that the waste form matrix and the near field engineered barriers (e.g. clay backfill, etc.), can successfully retain and prevent any migration to the far field environment for one thousand years and probably much longer (> 10^4 years). After the first thousand years the long lived nuclides such as ^{129}I, ^{135}Cs, ^{126}Sn, ^{99}Tc and ^{79}Se among the fission products and the actinides ^{234}U, ^{236}U, ^{237}Np, ^{239}Pu, ^{240}Pu, and ^{241}Am become the major concern.
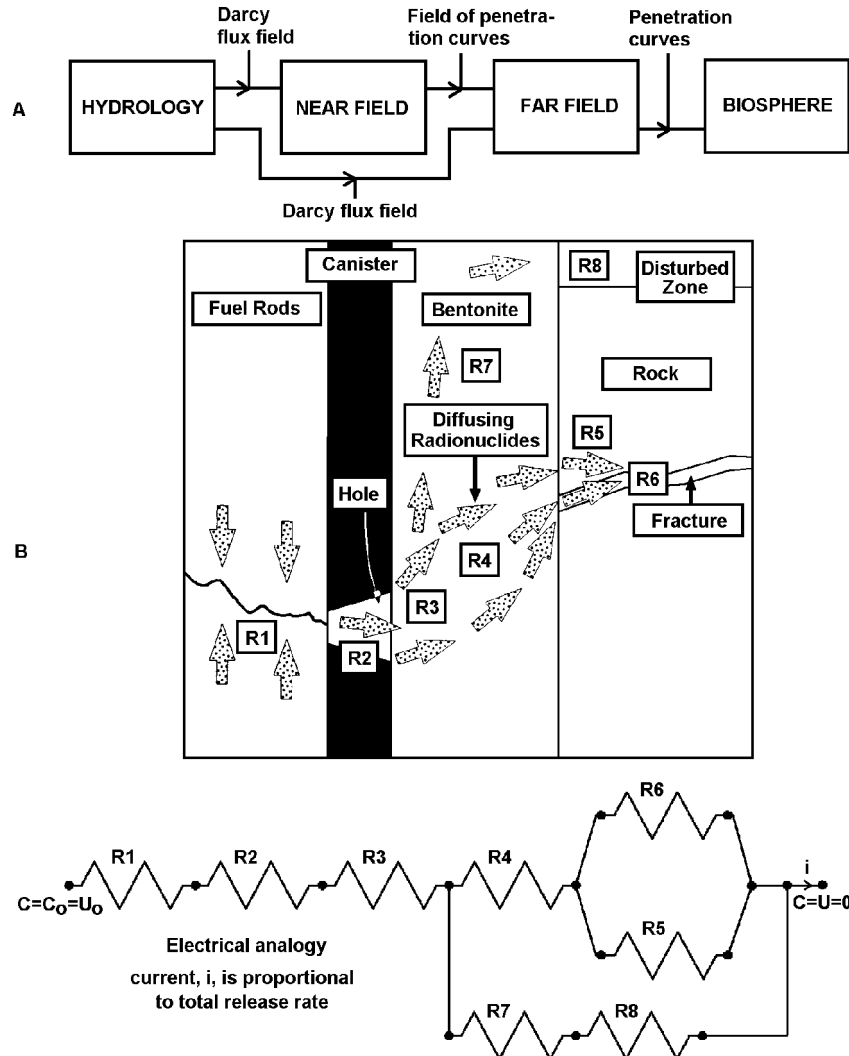
FIG. 22.10. Coupling of models in model chain for safety assessment of leakage of radionuclides from fractured fuel rod and canister in a bentonite filled rock hole. (SKB91).

22.10.1. *Release scenarios*

Two major types of scenarios are considered in the performance assessments for release of radionuclides from the repository. One scenario evaluates all the processes which are expected to occur normally in the region of the repository which could effect the rate of release and migration. In this scenario, ground water penetrates the waste packages and leaches the radionuclides which, then, can migrate through and out of the repository, Figure 22.10. R1, R2, etc represent mathematical models describing the migration of one particular radionuclide in that specific region. The Ri's are then added into the overall equation.

To assess the release by this scenario, it is necessary to evaluate the rate of release from the package, the flow rate of the underground fluids, the speciation and solubility of the different radionuclides and their diffusion (migration) rates.

The second scenario includes "disturbed" conditions which could be the result of geologic events such as earthquakes, volcanic activity and changes in hydrological conditions. This scenario also includes the effect of "human intrusion," in which people in future generations unknowingly penetrate a repository and release a portion of its radioactive contents to the earth's surface via the groundwater system. For example, this release could be the result of a drilling operation. Such events are assumed to occur over the history of the repository including some at very early times (less than 1 000 years). In this case, sorption and half-life and, for the most part, solubility are not major factors in determining the potential release. The dominant contribution would be from transuranic elements (mainly ^{239}Pu, ^{240}Pu, ^{241}Am) with some contributions from fission products.

22.10.2. *Canister dissolution*

The most common canister materials are copper and iron. In rocks, where the ground water is reducing (as e.g. in the Canadian and Scandinavian shields), copper is practically insoluble as shown by the existence of native copper, million years old, found in this environment. Detailed studies have shown that the radiation from the waste nuclides have a very small effect on the dissolution. It is therefore predicted that a 50 mm thick copper canister will be intact for at least one million years. Iron, or steel, can be expected to dissolve more rapidly, especially in oxidizing groundwater. However, the canister surrounding would become saturated by Fe(II), resulting in a reducing media, which would be important in limiting the waste nuclide migration.

TABLE 22.10. *Radionuclide solubilities and limiting phase in reducing and oxidizing Finnsjö fresh water* (SKB91)

|	Reducing conditions		Oxidizing conditions	
	solubility (M)	limiting phase	solubility (M)	limiting phase
Se	very low	M_xSe_y	high	-
Sr	1×10^{-3}	Strontianite	1×10^{-3}	Strontianite
Zr	2×10^{-11}	ZrO_2	2×10^{-11}	ZrO_2
Tc	2×10^{-8}	TcO_2	high	-
Pd	2×10^{-6}	$Pd(OH)_2$	2×10^{-6}	$Pd(OH)_2$
Sn	3×10^{-8}	SnO_2	3×10^{-8}	SnO_2
I	high	-	high	-
Cs	high	-	high	-
Sm	2×10^{-4}	$Sm_2(CO_3)_3$	2×10^{-4}	$Sm_2(CO_3)_3$
Am	2×10^{-8}	$AmOHCO_3$	2×10^{-8}	$AmOHCO_3$
Pu	2×10^{-8}	$Pu(OH)_4$	3×10^{-9}	$Pu(OH)_4$
Pa	4×10^{-7}	Pa_2O_5	4×10^{-7}	Pa_2O_5
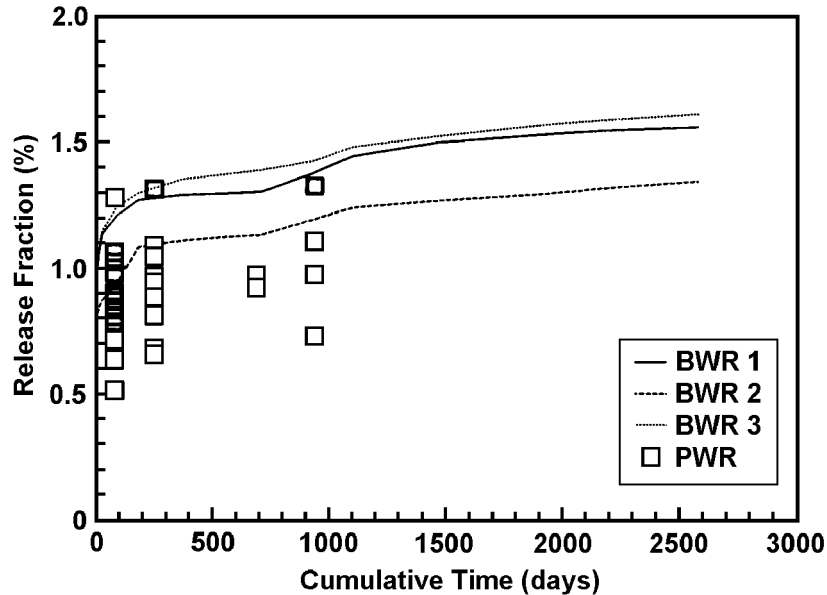
FIG. 22.11. Fraction of released cesium from BWR and PWR fuels in different waters as a function of contact time (SKB91).

As the metal encapsulation is dissolved or cracks (Figure 22.10.B), the radionuclides in the waste matrix (UO_2 or glass) will be released mainly with the dissolution rate of the matrix (*congruent dissolution*). A reasonable figure for the glass dissolution rate is 2×10^{-3} g m^{-2} d^{-1} exposed glass surface, assuming no limit with regard to the solubility product (i.e. unlimited amount of water); this corresponds to a corrosion rate of the glass surface of $\sim 2.7 \times 10^{-4}$ mm y^{-1}. Experience shows that this rate rapidly decreases with time. Thus strontium release rates were reduced by a factor of 10^6 in 15 y. Figure 22.11 shows measurements of the fraction of Cs released from spent fuel as a function of contact time with simulated ground water. By the time, the fuel matrix will be converted into hydrous oxide. The fraction altered has been measured under various conditions and are extrapolated to very long times in Figure 22.12. These results indicate that even if the barrier surrounding the canisters break down, the leakage of waste products into the near field would be quite small.

The dissolution rate of canister encapsulation and waste matrix is limited by water solubility. As mentioned above, of the actinides the most hazardous, plutonium, would most likely be in the +4 state and form a very insoluble hydroxide. This is particulary true in an Fe(II) environment caused by dissolution of an iron canister. Table 22.10 gives limiting solubilities and phases for the more important waste elements in reducing and oxidizing groundwater. Figure 22.13 shows the leakage rate from the near field of an initially defective canister, extrapolated to long times; all nuclides that are expected to leak out at a rate of more than 1 Bq y^{-1} are included in the Figure. In this prediction, the stipulations mentioned in the beginning of §22.10 are met.
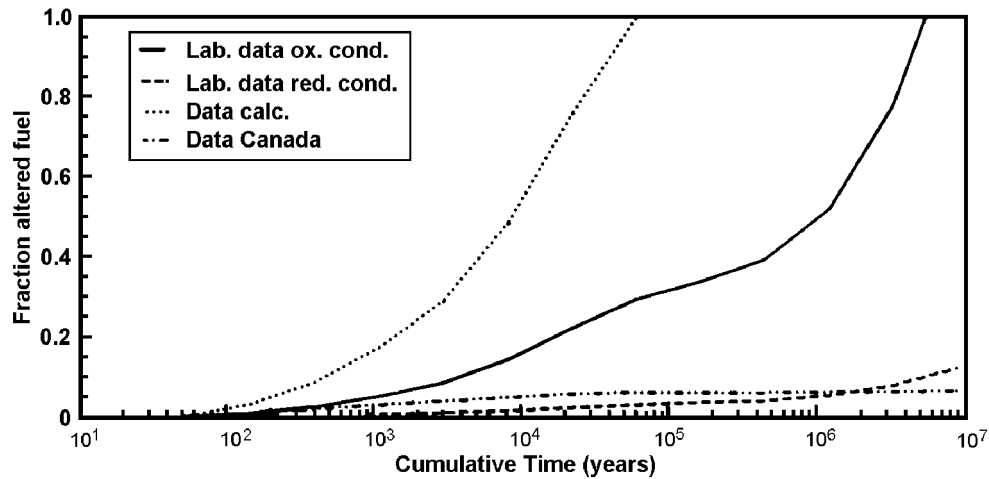
FIG. 22.12. Fraction of fuel altered in ground water as a function of time; the reaction is assumed to start 40 years after fuel discharge from the reactor (SKB91).

22.10.3. *Releases from bitumen and concrete encapsulations*

The low-level and intermediate-level wastes are to be encapsulated in bitumen, concrete or glass. The bitumen would be highly water resistant, but it ages with time and begins to lose strength in 10 – 20 years. Special bitumen materials have to be developed for wastes which must be contained in > 50 years. The bitumen drums are normally stored in a containment building, e.g. of concrete.

The groundwater surrounding concrete rapidly becomes very basic, pH> 13, as a consequence of leakage of Na^+ and K^+ ions. At a later stage, Ca^{2+} ions begin to leak, reducing the pH to about 10.5. Thus nuclides migrating through the concrete encounter very basic media, leading to the formation of insoluble hydroxides for most polyvalent ions, including all actinides. The leaching of Ca^{2+} from the concrete causes it to lose its mechanical strength and to begin to deteriorate. By suitable additives, the onset of deterioration can be delayed, and at pH< 10 the concrete is stable for very long times. However, concrete containers for LLW and MLW can not be considered to have an infinite lifetime, and therefore further containment is necessary.

22.10.4. *Migration from the repository*

After release into the near field, the radionuclides can only migrate via a water transport path (Figure 22.10). Migration in the far field may occur for radionuclides with long lifetimes, high solubility in ground water, and low sorption along the transport pathway. In repositories where the water is confined to interstitial fracture and pore areas, the

TABLE 22.11. *Far field radionuclide distribution values for granitic rock* (SKB91)

Element	k_d value $(m^3 kg^{-1})$	Element	k_d value $(m^3 kg^{-1})$
Zirconium	1	Carbon	0.001
Radium	0.15	Chlorine	0
Protactinium	1	Palladium	0.001
Thorium	2	Selenium	0.001
Uranium	2	Strontium	0.015
Neptunium	2	Cesium	0.15
Plutonium	0.2	Iodine	0
		Technetium	1

Conditions: specific surface area 0.1 m^2 per m^3 of rock, (equal to) 1 000 m^2 per m^3 of water; matrix diffusion coefficient 3.2×10^{-6} m^2 y^{-1}; diffusion porosity in the rock matrix 0.005.

actinides would have low solubility and high sorption compared with the fission products. All nuclides which adsorb would move slower than the free groundwater due to the

TABLE 22.12. *Individual doses and risks from intrusion scenarios in a granite repository of unreprocessed LWR spent fuel* (Mobbs et al.)

Radionuclide	100 years		100 000 years	
	Dose Rate $(Sv\ y^{-1})$	Risk[†] (y^{-1})	Dose Rate $(Sv\ y^{-1})$	Risk[‡] (y^{-1})
^{99}Tc	5.0×10^{-6}	1.5×10^{-14}	1.9×10^{-9}	2.5×10^{-14}
^{129}I	1.8×10^{-6}	5.4×10^{-16}	3.2×10^{-10}	4.2×10^{-15}
^{135}Cs	2.4×10^{-6}	7.0×10^{-15}	1.3×10^{-7}	1.7×10^{-12}
^{137}Cs	1.5	1.8×10^{-7}	- - -	- - -
^{234}U	7.3×10^{-4}	2.1×10^{-12}	5.0×10^{-7}	6.5×10^{-11}
^{235}U	1.8×10^{-5}	5.1×10^{-14}	1.4×10^{-6}	1.9×10^{-11}
^{236}U	1.9×10^{-4}	5.4×10^{-13}	2.8×10^{-7}	3.7×10^{-12}
^{238}U	2.0×10^{-4}	5.9×10^{-13}	5.9×10^{-7}	7.7×10^{-12}
^{237}Np	1.1×10^{-3}	3.1×10^{-12}	3.6×10^{-6}	4.7×10^{-11}
^{238}Pu	3.6	1.8×10^{-7}	5.1×10^{-6}	6.7×10^{-11}
^{239}Pu	1.0	1.8×10^{-7}	1.2×10^{-4}	1.5×10^{-9}
^{240}Pu	1.5	1.8×10^{-7}	3.1×10^{-7}	4.0×10^{-12}
^{241}Pu	1.0×10^1	1.8×10^{-7}	9.2×10^{-6}	1.2×10^{-9}
^{242}Pu	5.4×10^{-3}	1.6×10^{-11}	8.9×10^{-6}	1.2×10^{-10}
^{241}Am	2.0	1.6×10^{-7}	1.8×10^{-6}	2.4×10^{-11}
^{243}Am	6.4×10^{-2}	1.9×10^{-10}	3.4×10^{-6}	4.4×10^{-11}
^{244}Cm	8.7×10^{-2}	2.5×10^{-10}	4.7×10^{-9}	6.2×10^{-14}
^{245}Cm	4.8×10^{-4}	1.4×10^{-12}	7.3×10^{-9}	9.6×10^{-14}
Total	2.1×10^1	1.8×10^{-7}	1.6×10^{-4}	2.1×10^{-9}

[†] From S. F. Mobbs et al. [‡] Dose-risk conversion factor = 1.65×10^{-2} Sv^{-1} recommended by ICRP in 1977 [ICRP, 1977]. However, ICRP recommended a higher value, 5.0×10^{-2} Sv^{-1}, in 1990 [ICRP #60, 1990].
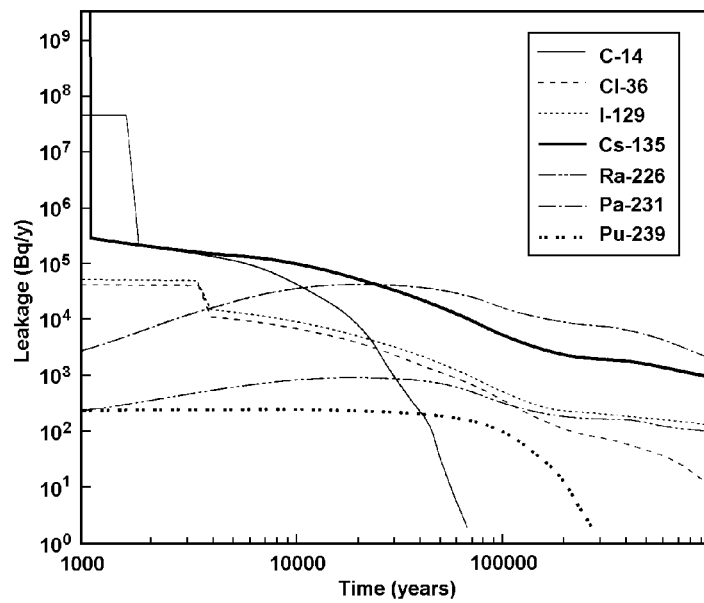
FIG. 22.13. Leakage from the near field of radionuclides from an initially defective canister; all nuclides that leak out at a rate of > 1 Bq/y are included (SKB91).

sorption-desorption equilibria. As a consequence ^{129}I and ^{99}Tc would be expected to be the principle contributors to a radioactivity release to the environment, as they are poorly adsorbed. This is also true for ^{14}C, which contributes because it is transported as dissolved CO_2 (Fig. 22.13).

The effect of elevated temperatures resulting from the energy released by the radioactive decay must be included in the evaluation of release and near field migration (i.e. within the repository volume). Elevated temperatures could alter the geology as well as the chemical speciation and solubility of the released nuclides. If the temperature exceeds the boiling point of water in the fluids, it would result in a drier repository with reduced or no release and migration.

When granite or clay is contacted with water containing dissolved cations, sorption or exchange of these ions with ions of the solid phase are observed. For example, montmorillonite has such a high exchange capacity that it is used as a natural ion exchanger, e.g. for water purification. The ion exchange elution curves in Figure 16.7, however, do not depend on sorption capacity, but on *sorption strength* and on *aqueous complexation*. The sorption strength depends on ionic charge (higher charged species sorb more strongly), ionic size (smaller ions sorb more strongly), etc., while aqueous complexation depends on the nature of the complexant (ligand), as well as on the cation properties.

All ground/soil/rock materials sorb ions, but the sorption distribution value (defined by k_d, eqn. (22.10)) depends on so many factors that they may be considered *site specific*; i.e. dependent on the ion released, the near field matrix composition (buffer material, dissolved canister, etc), the ground water composition and the rock mineral composition. However, clay and granite have about the same k_d values in similar groundwaters.
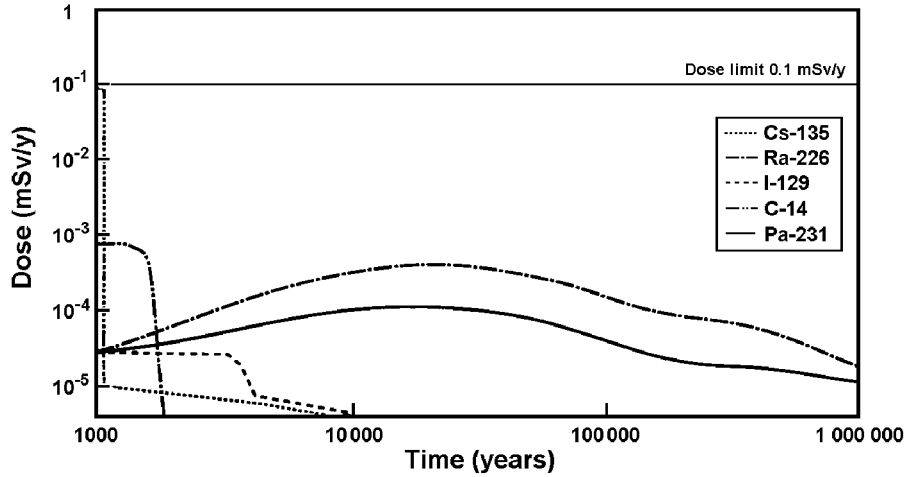
The distribution coefficient, k_d, is defined by

FIG. 22.14. Predicted dose rates to individuals from the release of a defective canister, assuming the release occurs directly to the biosphere, i.e. without retention in the ground (SKB91).

$$k_d = \frac{\text{conc. of radionuclide per kg soil/rock/etc}}{\text{conc. of radionuclide per m}^3 \text{ water}} \qquad (22.11)$$

Typical k_d values are listed in Table 22.11. From the k_d values and the soil and groundwater properties, the *retention time* for a radionuclide may be calculated. The radionuclide *retention factor* (*RF*) is defined as

$$RF = v_w/v_n = 1 + k_d \, \delta \, (1 - \epsilon) / \epsilon \qquad (22.12)$$

where v_w is the groundwater velocity (in granite typically 0.1 m y^{-1}), v_n the nuclide transport velocity (which must be $< v_w$), δ the soil density (typically 1 500 – 2 500 kg m^{-3}), ϵ the soil porosity (or void fraction, typically 0.01 – 0.05), The groundwater velocity can be obtained from eqn. (20.11), if geologic parameters are known. Observed k_d values for Swedish granite are given in Table 22.11. Typical retention times in granite are about 400 y for Cs, 1 500 y for Sr, 200 000 y for Ln(III) and 40 000 y for An(IV). Rather similar (within a factor of ten) values have been found for other geologic formations such as tuff from New Mexico, basalt from Idaho, and limestone from Illinois. The high retention values combined with a water transport time of a few years lead to retention of ^{90}Sr, ^{137}Cs, and most Pu, Am, and Cm isotopes over their lifetimes. With the negligible water flow rate through clay, diffusion is the dominating transport process. It is estimated that it will take 700 y for Cs, 1 800 y for Sr, 22 000 y for Am and 8 000 y for Pu to penetrate 0.4 m bentonite. During those times most of the radioactivity of these nuclides have decreased to negligible values. Studies for a salt repository (WIPP) in New Mexico indicate that, of all waste nuclides released in the repository, only ^{14}C, ^{99}Tc, and ^{129}I may

reach the surface before they have decayed. Thus, ground retention of the radionuclides plays an essential role in the risk evaluation.

Both dissolution rate and transport rate of nuclides depends on the existence of complex formers in the groundwater. Such complex formers are Cl^-, F^-, SO_4^{2-}, HPO_4^{2-}, CO_3^{2-}, and organic anions (e.g. humic acid). Complexes with these anions, in most cases, increase solubility, and – through formation of less positively charged metal species – reduce the retention factors. The groundwater conditions, therefore, play a central role in evaluation of the risks of a waste repository. Since these conditions vary, they have to be evaluated for each site. This point is illustrated by the Maxey Flats facility in the USA, where radionuclides were found to move from a storage basin much more rapidly through soil than would be expected from the equations above. This was found to be caused by the addition of strong metal chelating complex formers like diethylenetriaminopentaacetic acid (DTPA) to the basin liquid. The DTPA complexes have negative charge, resulting in lower k_d values (usually ~ 1). This reflects the necessity to know in adequate detail the chemistry of the waste and of the storage site for proper evaluation of the safety.

Figure 22.14 shows the result of a safety analysis, indicating the estimated amounts of released radioactivities carried by ground water from a spent fuel repository to a recipient, and the expected doses delivered, without consideration of retention. Retention will cause the ^{226}Ra and ^{231}Pa to reach zero value before 10 000 years.

Calculations for individual doses and the risks for intrusion into a granite repository of LWR spent fuel at 100 and at 100 000 years after burial are listed in Table 22.12. These calculations are based on very extensive modelling (cf. Fig. 22.10) of the releases and uptakes from wastes produced from a 20 GW$_e$ reactor park operating in Europe for 30 years, including reprocessing and storage of LLW and ILW in surface facilities, and HLW, either in the form of spent fuel elements or vitrified HLLW in an underground granite repository. To model the dissolution of radionuclides and their migration in the ground existing facilities in their actual environments have been chosen. Similarly, for the uptake actual food chains (crops, fish , etc and eating habits) have been used. The quantity of spent fuel is assumed to be 18 000 t IHM. The LLW and ILW repositories are assumed to begin to leak at time 0, the dissolved radionuclides migrating into the actual soils, reaching streams and wells, etc, while it is assumed that the spent fuel elements or high level waste glass begins to leak after 1 000 years. The radionuclides migrate by groundwater under various retention conditions, depending on hydrogeologic conditions and chemical properties. The exposed population is divided into four groups: the critical group around the installations, the population of the country, the population in Europe and in the world. As expected, the population dose is the highest for the critical and national groups for aqueous releases, but about the same for all groups for gaseous releases. The model also includes an intrusion scenario using a well drilling probability, beginning after 300 years (in the main case), as it is expected that control will last that long. It is assumed that as soon as a drill core from a waste repository is taken, it will immediately be recognized; this means that high doses from the core will only be received by drilling and laboratory personal. The risk from intrusion after 100 years is calculated to be 8.1×10^{-7} y^{-1} and after 100 000 years 2.1×10^{-9} y^{-1}. By comparison, the calculated risk from the "normal" scenario of releases from spent fuel elements and migration in the environment over a long period is 5×10^{-5} y^{-1}. With this exception all the maximum calculated individual risks from disposal of solid wastes are below the limit of 10^{-5} y^{-1} recommended by the ICRP. For

vitrified high level waste and spent fuel disposal, the doses calculated for intrusion scenarios are very high but the probability of occurrence are low, so the risks from intrusion are lower than those from radionuclide migration with groundwater. The maximum individual doses from the migration scenarios for solid waste disposal are predicted to arise beyond 10 000 years after closure of the repository.

These values indicate that release and migration is the more significant concern, although even for this scenario, geologic disposal is calculated to present very small risks to future generations.

22.11. Conclusions

A rather large amount of nuclear fission products and actinide elements have been released to the environment from nuclear weapons testing and from accidental and intentional discharges from nuclear reactor operations and fuel reprocessing. The research on the fate of these released radionuclides suggest that the long lived actinides form quite insoluble or strongly sorbed species while ^{129}I and ^{99}Tc have relatively high dissemination in natural systems. The most active shorter-lived species (^{90}Sr, ^{137}Cs) also have more mobility in ecosystems.

These conclusions are confirmed by the results of the investigations of radionuclide behavior in natural analog sites. Even more relevant are the results of the natural reactor region at Oklo.

The data from field studies is largely confirmed by the performance assessments of proposed nuclear waste repositories. The "intrusion" scenario is calculated to have a lower risk than the undisturbed natural leach and migration scenario. The latter qualitatively agrees with the Oklo data and indicates no unacceptable risks result from a carefully chosen and designed geologic repository in which the nuclear wastes are emplaced with appropriate packaging.

22.12. Exercises

22.1. What is the purpose of the clay buffer of a waste repository in granitic rock?

22.2. Which of the following ions move slower than the groundwater: K^+, Cs^+, La^{3+}, TcO_4^-, HCO_3^-?

22.3. Why is Np assumed to move faster than Pu in most groundwaters?

22.4. (a) What types of geologic formations are considered for waste repositories? (b) Which types are used/planned for Asse and WIPP?

22.5. What will be the concentration of $Am(CO_3)_2^-$ at pH 7 under the conditions given in §22.7.

22.6. What will be the ratio of [Pu(III)]/Pu[(IV)] in a groundwater containing small concentrations of iron in the relation Fe(II) 99% and Fe(III) 1%? $E^{\circ}_{Fe(II)/Fe(III)} = 0.743$ V. Neglect hydrolysis.

22.7. (a) Calculate the Pourbaix-line for Np(IV)/Np(V) in Figure 22.4. (b) What value must the Eh value of water exceed at pH 6 for Np(V) to dominate? Neglect hydrolysis.

22.8. A miner has a deep well 160 km away from a waste repository. During an earthquake, the rock fractures and a groundwater stream opens between the repository and the well so that 10 Ci ^{90}Sr momentarily dissolves and moves toward the well at v_w 160 km y^{-1}. (a) What will be the amount of ^{90}Sr (in Bq) reaching the well (assume plug flow)? (b) Will that water be harmful to the miner?

22.13. Literature

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