

TECHNICAL REPORTS SERIES NO. 445

# **Applicability of Monitored Natural Attenuation at Radioactively Contaminated Sites**



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International Atomic Energy Agency

APPLICABILITY OF MONITORED  
NATURAL ATTENUATION  
AT RADIOACTIVELY  
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TECHNICAL REPORTS SERIES No. 445

# APPLICABILITY OF MONITORED NATURAL ATTENUATION AT RADIOACTIVELY CONTAMINATED SITES

INTERNATIONAL ATOMIC ENERGY AGENCY  
VIENNA, 2006

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## FOREWORD

The IAEA attaches great importance to the dissemination of information that can assist Member States with the development, implementation, maintenance and continuous improvement of systems, programmes and activities that support a sustainable nuclear fuel cycle and nuclear applications, including managing the legacy of past practices and accidents. Hence, the IAEA has initiated a comprehensive programme of work covering all aspects of environmental remediation including:

- Technical and non-technical factors influencing decision making in environmental remediation;
- Site characterization techniques and strategies;
- Assessment of remediation technologies;
- Assessment of technical options for cleanup of contaminated media;
- Post-restoration compliance monitoring;
- Assessment of the costs of remediation measures.

It has been observed that many measures to remove or contain contamination are inefficient below certain concentrations, in general costly, and of a limited lifetime compared with the half-lives of the radionuclides concerned. Dispersed low level contamination poses a particular challenge to those charged with its remediation. Economic considerations in many Member States also result in constraints being placed on resources available to deal with such contamination. Experience has also shown that many techniques are not efficient below certain concentration thresholds or may entail impacts on certain environmental compartments in addition to those due to the contamination itself. This includes doses received by workers on the remediation project. As a result, the concept of relying on geological media to retain contaminants and/or to ‘flatten out’ concentration/dose peaks is increasingly being discussed in a remediation context.

Technical Reports Series No. 424 (Remediation of Sites with Dispersed Radioactive Contamination) examined a variety of technological options for remediating dispersed contamination and concluded that the approaches can be broadly grouped into three categories: non-intervention, containment and removal.

This report discusses in detail the necessary prerequisites, processes involved and applicability of non-intervention as a strategy for dealing with radioactive contamination. Particular emphasis is put on modelling tools as integral elements of monitored natural attenuation (MNA). It provides a comprehensive critique of, and explores the limits of, the applicability of MNA.

While MNA is de facto relied upon in many instances where contamination cannot be completely removed from an engineered repository, it is emphasized that non-intervention is not equivalent to a 'do nothing' option. In order to rely on MNA safely, a thorough understanding of the site and the migration behaviour of the contaminants in the given environment is needed. This is gained from a comprehensive site investigation. This report complements other recent reports on remediation techniques and strategies with a less invasive concept.

An extensive body of references including relevant web sites will help the reader to find more detailed or more up-to-date information.

The work on the technical publication was organized and the final report compiled by W.E. Falck of the Division of Nuclear Fuel Cycle and Waste Management.

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# 1. INTRODUCTION

## 1.1. BACKGROUND

Responding to the needs of its Member States, the IAEA has launched an environmental remediation project dealing with the problems of radioactive contamination worldwide. Its aim is to collate and disseminate information concerning the key problems affecting the environmental remediation of contaminated sites (Table 1) [1–18].

The term ‘remediation’ is used here to encompass all activities leading to a reduction in radiation exposure and to an improvement in the environmental and/or economic value of a site. It does not necessarily imply restoration of pristine environmental conditions but rather the management of contamination either by removal, fixation or monitoring.

It has been observed that many measures used to remove or to contain contamination are inefficient below certain concentrations, in general costly, and of a limited lifetime compared with the half-lives of the radionuclides concerned. Dispersed low level contamination poses a particular challenge to those charged with its remediation. Economic constraints in many Member States result in limited resources being available to deal with such contamination. Experience has shown that application of intrusive techniques may have other environmental impacts or expose workers on the remediation project, leading to unacceptable doses [19].

The concept of ‘natural attenuation’ has received a great deal of attention in recent years [20–26] and forms the subject of a US Environmental Protection Agency (USEPA) directive [27]. Assessments of sites contaminated with degradable organic contaminants invariably factor in this effect and this approach is increasingly being considered for heavy metals [18, 28]. With only a few exceptions, the most common radioactive contaminants in the environment are also heavy metals and, in principle at least, it follows that the same considerations given to heavy metals should apply to radioactive contaminants. Indeed, given the fact that radioactive decay is an inherent attenuation mechanism, the approach could be regarded as even more relevant in this case. To date, however, monitored natural attenuation (MNA) has not been advocated specifically for radioactively contaminated sites.

A wealth of experience in remediation measures for radioactively contaminated land has been gained since the Chernobyl accident [29]. An emerging theme from this work is that the focus should be moved towards low cost, low intensity ‘passive’ or low maintenance solutions [16, 18] rather than intrusive, and usually expensive, engineering techniques. In situ containment

TABLE 1. RELEVANT TOPICAL PUBLICATIONS PRODUCED OR UNDER DEVELOPMENT

Safety	Management	Databases	Technology	Special topics
Management of Radioactive Waste from the Mining and Milling of Ores [1]	Factors for Formulating Strategies for Environmental Restoration [2]	A Directory of Information Resources on Radioactive Waste Management, Decontamination and Decommissioning, and Environmental Restoration [3]	Technologies for Remediation of Radioactively Contaminated Sites [4]	Extent of Environmental Contamination by Naturally Occurring Radioactive Material (NORM) and Technological Options for Mitigation [5]
Monitoring and Surveillance of Residues from the Mining and Milling of Uranium and Thorium [6]	Characterization of Radioactively Contaminated Sites for Remediation Purposes [7]	Design Criteria for a Worldwide Directory of Radioactively Contaminated Sites (DRCS) [8]	Technical Options for the Remediation of Contaminated Groundwater [9]	The Long Term Stabilization of Uranium Mill Tailings [10]
Remediation of Areas Contaminated by Past Activities and Accidents [11]	Compliance Monitoring for Remediated Sites [12]	A Worldwide Directory of Radioactively Contaminated Sites (DRCS), <a href="http://www-drcs.iaea.org">www-drcs.iaea.org</a>	Site Characterization Techniques Used in Environmental Restoration Activities [13]	Applicability of Monitored Natural Attenuation at Radioactively Contaminated Sites (this report)
Removal of Sites from Regulatory Control on Termination of Practices [14]	Non-technical Factors Impacting on the Decision Making Processes in Environmental Remediation [15]		Remediation of Sites with Dispersed Radioactive Contamination [16]	
	Management of Long Term Radiological Liabilities: Stewardship Challenges [17]		Remediation of sites with Mixed Contamination of Radioactive and Other Hazardous Substances [18]	

methods preventing direct exposure or uptake via the food chain have proved successful, particularly in the case of the short lived nuclides [30].

All significant remediation programmes for radioactively contaminated land will be subject to an environmental impact assessment. This will incorporate, among other activities, the results of geological, hydrogeological and geochemical surveys of the site(s), performance modelling and post-remediation monitoring, the latter to demonstrate compliance with the relevant regulations. The aim of the environmental impact assessment is to assist in selection of the remediation approach and to establish the safety of the option chosen.

In each case, reliable models are required of the likely fate of contaminants for various exposure scenarios and potential exposure pathways in order to justify the remediation strategy chosen. Such models rely, in turn, on an adequate understanding of geochemical dispersion and accumulation mechanisms.

Whether or not MNA is adopted as the preferred route, the principles governing long term environmental protection need to take into account the natural background. In the case of naturally occurring nuclides, there is always a local background level against which cleanup goals and/or regulatory target values should be evaluated. This is a fundamental difference to remediation of xenobiotic organic contaminants where 'natural' background is zero.

Time-frame is another important consideration when deciding on performance measures. The regulations used to judge the acceptability of an underground repository for nuclear waste, for example, are invariably based on dose and/or risk. The most commonly used measure is radiological risk. In Finland, where the spent fuel disposal programme is advanced, an effective annual dose of 0.1 mSv for the most exposed individual is taken as the limit. Similar constraints are now being employed when devising remediation targets for radioactively contaminated land or former uranium mining areas. The choice of these measures, though routine with operational nuclear plant, causes many problems in an environmental context, since:

- (a) There is great controversy surrounding the health effects of prolonged exposure to low doses of ionizing radiation;
- (b) Local factors are not easily taken into account, as natural background varies substantially within and between countries;
- (c) Assumptions need to be made concerning site evolution and future human behaviour that are almost impossible to justify;
- (d) Neither dose nor risk are concepts easily understood by non-technical audiences;

- (e) There are a number of shortcomings with existing performance assessment models.

For these reasons, the IAEA, amongst others, has initiated research into alternative indicators of safety that may be used as an adjunct to dose and risk, particularly over longer time-frames [16, 31]. Several countries have embraced the concept of employing natural geochemical concentrations or fluxes [32]. Such an approach offers the advantage of comparing the results of safety calculations directly with natural sources of exposure to ionizing radiation. The processes leading to contaminant migration and retention can be treated explicitly in mechanistic models, as discussed below.

This report discusses: (a) the mechanisms effecting natural attenuation as a factor of the geosphere media and radionuclides; (b) the applicability or otherwise of natural attenuation strategies at sites contaminated by radioactivity; (c) uncertainties in parameter estimation; (d) MNA assessment methods including coupled transport modelling and (e) related monitoring requirements. The report discusses the terrestrial environment only.

## 1.2. THE PRINCIPLE OF MNA

Natural attenuation, by definition, constitutes the least invasive approach to environmental remediation. The concept is not new. For example, it forms an integral component of the design criteria for geological repositories that depend on geochemical processes to retard radionuclide migration to the biosphere [33, 34]. Neither is it entirely without financial cost. Reliance on natural attenuation requires detailed characterization of the site and adequate monitoring owing to the evolution of natural systems with time and to our incomplete understanding of the processes operating. The effects of any change in land use or in water extraction also need to be assessed. Hence, this strategy is usually termed MNA [27, 35, 36], to distinguish it from ‘walk-away’ situations (Fig. 1).

The purpose of MNA is to take advantage of natural processes that reduce the flux of a contaminant reaching any given receptor. It represents a form of temporal dilution, which should not be confused with the physical dilution that takes place, for example, when activity is discharged into water courses and dispersed. The time-frame over which the retardation process occurs is all-important and depends on the half-life of the nuclide. For those species with half-lives of the order of a few years or decades the success of the strategy can be verified directly by monitoring the site. Clearly, in the case of

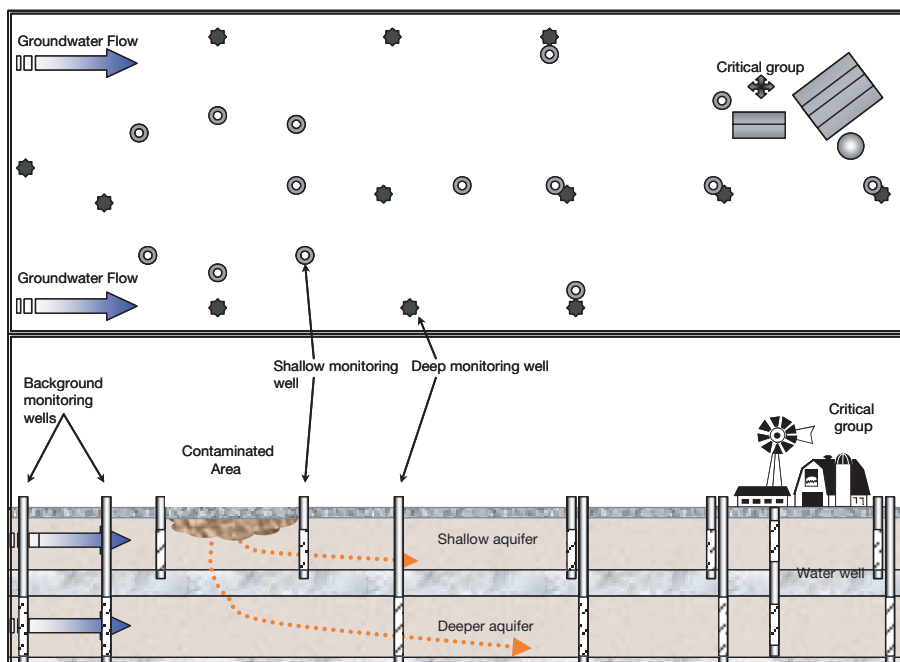


FIG. 1. The principle of MNA.

long lived nuclides this is not possible and so monitoring conveys a somewhat different meaning. It needs to be carried out for sufficient time to demonstrate proof of concept, after which time models are used to extrapolate the findings over more protracted timescales. Since conditions are likely to change over time, the likely impact of these changes must be assessed.

Targets may be defined for MNA in much the same way as they would be for any remediation strategy [11]. Notwithstanding public concerns regarding ionizing radiation, the targets need to be realistic. Uranium and thorium series nuclides occur naturally and background varies between and within countries. In the case of mine wastes, background in the immediate vicinity of the mining site will be high and this would have to be taken into account.

The USEPA states that “MNA should not be considered a default or presumptive remedy at any contaminated site” [27]. However, given an adequate site investigation and risk assessment programme, MNA can be considered a baseline option, against which other, active remediation options are compared with respect to performance, cost and residual risk.

It may be noted in this context that frequently active remediation measures are initiated without the same level of site investigation as that



required for MNA and with the consequent failure or cost overruns of projects. It may also be noted that in cases where it is difficult to establish an adequate monitoring programme, for example, owing to the complexity of the geological system, it will be equally difficult to make the necessary site assessments for other remediation methods with confidence. The degree of confidence that can be ascribed to natural attenuation in preventing harmful exposure or environmental damage is proportional to the level of characterization of that site. Developing an understanding of the physical, chemical and biological processes operating is more crucial in the case of natural attenuation than if the contamination were to be removed physically from the site. At the same time it is important to consider that the site for a final repository of such remediation wastes must fulfil similar criteria concerning its long term stability.

A decision to apply MNA as the preferred management strategy will invariably be made by considering a combination of scientific, economic and social criteria. Ideally, it should be based on a prior risk analysis of the specific site and follow an established technical protocol [37]. A quantitative decision making tool will help to balance objectively the advantages and disadvantages mentioned above [15]. Models exist for evaluating the likely performance of such systems, for designing the monitoring programme and for interpreting the monitoring data [38, 39].

### 1.3. SOURCES OF CONTAMINATION

Activities and events that have caused radioactive contamination include: nuclear reactor accidents; activities related to the nuclear fuel cycle (such as uranium mining and milling of metalliferous and non-metalliferous ores); production of non-nuclear fuels, including coal, oil and gas; production of industrial minerals, including phosphate and clay materials; and failures in the waste containment system [5]. In addition to the above, weapons testing, including the use of depleted uranium, has led to widespread radioactive contamination.

## 2. MIGRATION AND RETENTION MECHANISMS

### 2.1. OVERVIEW

Attenuation in its strict sense means ‘reduction’. However, unlike in the case of biodegradable organic contaminants, the majority of processes discussed in this report do not actually reduce the total mass of radionuclides in a given system, rather, they affect their distribution over space and time. The only exception is radioactive decay.

A large number of processes affect the migration of radionuclides in the geosphere, and these are discussed in the following sections. In order to be utilized for MNA, these processes must prevent or delay the arrival of a radionuclide at a receptor until such time that they have decayed to levels of no concern.

It is important to note that many of the geochemical and biological processes discussed may effect retardation, but at the same time these can lead to a reconcentration of radiologically relevant elements, which can then form potential secondary sources of contamination [25].

### 2.2. RADIOACTIVE DECAY

The half-lives of radionuclides now present in the environment range from microseconds to many millions of years. For higher members of the natural series ( $^{234/235/238}\text{U}$ ,  $^{232}\text{Th}$ ) together with some transuranics and fission products (e.g.  $^{99}\text{Tc}$ ,  $^{129}\text{I}$ ), no substantial decay will have occurred even over the longest assessment time-frames. However, many other isotopes produced by nuclear fission (e.g.  $^{60}\text{Co}$ ,  $^{90}\text{Sr}$ ,  $^{137}\text{Cs}$ ) or contained in industrial NORM will not persist beyond a few hundred years. The extreme fractionation between members of a decay series caused by chemical processing precludes the assumption of secular equilibrium in the majority of cases [40]. Clearly, therefore, it is essential that a detailed radionuclide inventory be compiled before deciding to adopt MNA as a management policy at any given site.

## 2.3. PHYSICAL PROCESSES

### 2.3.1. Introduction

Physical processes involved in natural attenuation (advection, diffusion, dispersion) may dilute radioactive contamination or partially remove/relocate and spread it (wash-off, erosion, resuspension, volatilization and subsequent atmospheric transport). This section presents basic physical processes of natural attenuation and approaches for their modelling. All of these processes have been intensively studied in relation to general geophysics, hydrology and atmospheric physics or in the context of radiation protection and radionuclide migration in the environment [41–43]. Substantial progress in this direction has been made in the years since the Chernobyl accident [44, 45]. The IAEA has released a number of manuals and handbooks on subject areas that are closely related to the subject of MNA [46–48].

### 2.3.2. Advection, diffusion, dispersion

The effect of the physical and some of the physicochemical processes on migration, concentration and distribution of radionuclides is summarized in Fig. 2.

#### 2.3.2.1. Advection

The term advection describes the movement of solutes and suspended matter with the ground- and pore water flow. In porous aquifers, this non-turbulent, laminar flow follows Darcy's Law, which defines the specific discharge as a product of the hydraulic conductivity coefficient  $k_f$  and the hydraulic gradient  $J$ . Assuming homogeneity and isotropy of the porous medium:

$$V_f = k_f J \quad (1)$$

The effective velocity  $V_e$  is the mean transport velocity between two points in the aquifer and results from the filter velocity ( $V_f$ ) and the relative effective porosity  $N_e$ :

$$V_e = V_f / N_e \quad (2)$$

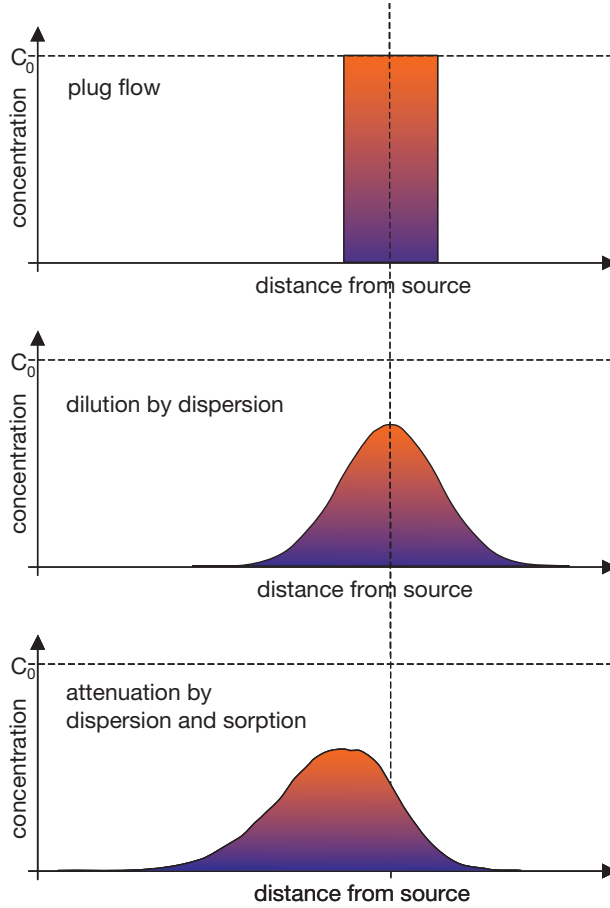


FIG. 2. Illustration of selected transport mechanisms effecting dilution and attenuation.

#### 2.3.2.2. Dispersion

Mechanical or hydrodynamic dispersion describes the macroscopic phenomenon whereby dissolved constituents, as well as suspended particulates and colloids, are transported with different velocities and in different directions along the flowpath as a result of inhomogeneities in porous media. This dispersion is caused by movement through the pores at variable velocities and in different directions and results in a longitudinal, transverse and vertical

dispersion of the transported solutes and solids. The dispersion coefficient  $D_M$  can be estimated from the dispersivity  $\alpha$  and the effective velocity  $V_a$  [49]:

$$D_M = \alpha V_a \quad (3)$$

Dispersion is generally higher in the flow direction (longitudinal) than in the direction perpendicular to the flow (transversal and vertical). It increases with increasing flow length.

#### 2.3.2.3. Diffusion

The distribution of contaminants in solution undergoes molecular diffusion, i.e. it follows the concentration gradient. The flux through a surface is described by Fick's first law [49]:

$$F = -D_d \cdot \delta_c / \delta_x \quad (4)$$

where  $F$  is the diffusive flux ( $\text{mol} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$ ),  $D_d$  is the diffusion coefficient ( $\text{cm}^2 \cdot \text{d}^{-1}$ ),  $\delta_c / \delta_x$  is the concentration gradient ( $\text{mol} \cdot \text{cm}^{-3} \cdot \text{m}^{-1}$ ), and  $c$  is the concentration in the pore fluid ( $\text{mol} \cdot \text{cm}^{-3}$ ).

In diffusive transport in porous media, the pathway around grains also has to be included in order to estimate the effective diffusion coefficient  $D^*$ :

$$D^* = \omega D_d \quad (5)$$

where  $\omega$  is an empirically determined parameter [49].

#### 2.3.3. Soil erosion and wash-off

Surface run-off from contaminated land is one of the major processes responsible for the contamination of water bodies. Surface run-off effects two processes: the wash-out of contaminants in dissolved form and the wash-off of sediment particles. Wash-off is the result of various erosion processes and is relevant for contaminant transport since contaminants can become attached by sorption to the surface of particles or may otherwise be bound onto or locked into the particles. The magnitude of surface run-off and, hence, wash-out is controlled by a variety of factors and processes [41]. Hydrologists distinguish a variety of flows resulting from precipitation reaching the ground:

- (a) Run-off, which is made up of various components including overland run-off, interflow and groundflow;

- (b) Infiltration, which is the amount of precipitation reaching the ground minus the various types of run-off. The amount infiltrating depends on the drainage properties of the soil, which in turn depend on its prior water saturation, grain size distribution, humus content, etc.

While the processes are well understood in principle, they may be difficult to determine in their magnitude for a given event or area, e.g. a catchment area. Their magnitude depends on a range of additional variables, including:

- (a) Magnitude, duration and form (rain, snow, etc.) of precipitation events;
- (b) Interception of the precipitation by the canopy, where evaporation reduces the amount of water reaching the ground;
- (c) Formation of snow layer and snow melt processes that tend to result in less overall run-off than that due to rainfall;
- (d) Run-off retention and loss in surface depressions, as water from small puddles tends to evaporate more quickly;
- (e) Evapotranspiration, which is the sum of evaporation processes from the soil surface and profile and transpiration by the vegetation cover. Plant roots may reach deep into the soil and remove already infiltrated water.

The erosion resistance of a soil depends, not least, on the vegetation cover. In addition to reducing the actual run-off by the processes discussed above, the plant roots 'keep the soil together'. Anthropogenic changes to the vegetation cover, for example, by clearance logging and ploughing of pastures, can dramatically increase soil erosion rates.

In addition to being controlled by the above hydrological processes, soil erosion is also governed by the processes involving the dissipation of the kinetic energy of rain drops in dislodging soil particles from their structure, thus facilitating their wash-out. It is customary to distinguish the following mechanisms of soil erosion [50]:

- (a) Splash detachment and soil splash transport action caused by rain droplets;
- (b) Soil detachment and soil transport of interrill or sheet flows;
- (c) Soil detachment and soil transport of rill flows of overland run-off and subsurface run-off.

The following catchment properties control the soil erosion process [42, 51]:

- (a) Physical structure and chemical properties of soil;
- (b) Properties of liquid precipitation (size and energy of droplets, time distribution of rainfall intensity);
- (c) Hydrodynamic properties of surface and subsurface flows;
- (d) Relief of catchment area;
- (e) Land use, land cover and agricultural practices;
- (f) Seasonal characteristics of vegetation cover in the catchment area.

In addition to the above factors, the erosion behaviour also depends on the soil sedimentology, i.e. mainly on the grain size distribution and the mineralogy.

A quantitative measure of radionuclide loss from a catchment is the wash-off coefficient ( $K_w$ ). The fraction of total supply of a radionuclide to a catchment area leaving as wash-off with solid particles is referred to as the 'solids' wash-off coefficient ( $K_s$ ) and that washed off in dissolved form is the 'liquids' wash-off coefficient ( $K_l$ ):

$$K_s = \frac{\int_0^T C_a(t)m(t)dt}{\int_s C_s ds} = \frac{C_a^* M}{C_s^* S}; \quad K_l = \frac{\int_0^T C_w(t)v(t)dt}{\int_s C_s ds} = \frac{C_w^* V}{C_s^* S} \quad (6)$$

where:  $C_w(t)$ ,  $C_w^*$  are instantaneous and weighted average concentrations of a radionuclide in the run-off (Bq/L), respectively;  $C_a(t)$ ,  $C_a^*$  are instantaneous and weighted average specific activities of a radionuclide on suspended particles (Bq/g), respectively;  $m(t)$  is the intensity of wash-off for suspended particles (g/s);  $M$  is the total weight of washed-off particles (g);  $v(t)$  is the run-off intensity (L/s);  $V$  is the total run-off volume (L);  $C_s$  is the surface density of contamination (Bq/m<sup>2</sup>);  $C_s^*$  is the surface density of pollution averaged over a watershed (Bq/m<sup>2</sup>);  $S$  is the watershed area (km<sup>2</sup>);  $0, T$  are starting and termination times (s) of a run-off, respectively; and  $t$  is the time (s).

By dividing  $K_l$  by run-off depth and  $K_s$  by the amount of suspended matter washed off from a unit soil surface, normalized coefficients of 'liquid' ( $K_l^*$ ) and 'solid' ( $K_s^*$ ) wash-off are obtained, which are equal to the ratio of a corresponding weighted average concentration and average density of pollution in a catchment area:

$$K_l^* = \frac{K_l}{h} = \frac{K_l S}{V} = \frac{C_w^*}{C_s^*}; \quad K_s^* = \frac{K_s}{q} = \frac{K_s S}{M} = \frac{C_a^*}{C_s^*} \quad (7)$$

where  $h$  is the run-off depth (mm) and  $q$  is the suspension mass washed off from a unit watershed area.

The expected run-off depth multiplied by  $K_l^*$  and the expected removal of suspended material multiplied by  $K_s^*$  can be used for predicting the input of radionuclides into rivers in solution and bound to suspended particles, respectively.

Some experimentally determined wash-off coefficients for a selection of radionuclides are given in Table 2 [51, 52] and these indicate the magnitude of secondary contamination of water bodies by surface run-off from contaminated catchment areas.

The amount  $m$  of soil eroded during a rainfall event on a catchment area is given by [50, 51]:

$$m = h^n abk \quad (8)$$

which is dependent not only on the run-off depth  $h$ , but also on the parameters  $n$ ,  $a$ ,  $b$  and  $k$  which are indicators of the type of erosion process, soil type and landscape, agricultural practices and slope in the catchment area.

TABLE 2. WASH-OFF COEFFICIENTS OF SOME RADIONUCLIDES IN EXPERIMENTS FROM CHERNOBYL

Radionuclide	Mean annual wash-off coefficient $K_w$ ( $10^{-3}/a$ )	$K_w^*$ ( $10^{-5}/mm$ )
$^{90}\text{Sr}$	2–6	10–20
$^{106}\text{Ru}$	1–2	0.2–0.7
$^{125}\text{Sb}$	0.3–1	—
$^{134,137}\text{Cs}$	1–4	0.3–5
$^{144}\text{Ce}$	0.5–1	0.2–0.6
$^{60}\text{Co}$	0.5–1	0.2–0.6
$^{239}\text{Pu}$	0.1–0.5	0.1–0.2



#### 2.3.4. Sedimentation and erosion

Sedimentation and erosion are ubiquitous processes occurring in surface waters. The transport behaviour and dispersal of contaminants bound onto or within particles, in addition to being subject to chemical interaction with the surrounding aqueous phase, are controlled by the processes that control the movement of the particles themselves [51, 53]. Hence, sedimentation and resuspension become important transport processes to consider.

Accumulating sediments can result in areas with increased contamination levels. These areas, under certain conditions of hydrodynamic flow, may become a source of secondary contamination when sediments are resuspended by erosion from the bottom [42].

The transport of suspended solids is often visually detectable as turbidity. Larger particles are not transported in suspension, but roll or jump along the bottom surface, a mode of transport not so easily observed. Both bottom sediment transport and suspended sediment concentrations increase exponentially with water flow velocities [41].

There are conceptual differences in the erosional behaviour of cohesive and non-cohesive sediments. A comprehensive treatment of erosion mechanisms and their dependence on grain size distributions, grain shape, bottom surface roughness and topography, and the sediment mineralogy is beyond the scope of this report. The reader is referred to standard textbooks on sedimentology [54]. It may suffice here to state that the erosional behaviour of clayey sediments, which are important substrates for the sorption of radionuclides, is rather complex owing to the cohesive properties of clays.

Sedimentation in still water can be described in relatively simple terms, depending mainly on the viscosity of the water, the shape of the particles and their specific gravity. Flow, and in particular turbulent flow, complicates matters because of the shear forces acting on particles and the surface of the accumulating sediment.

Radionuclide deposition due to sedimentation from a motionless water column can be written as:

$$R = K_d S_{\downarrow} \frac{\partial c}{\partial z} \quad (9)$$

where  $S_{\downarrow}$  is the accumulation rate of particles with radionuclides bound to them [51] and  $K_d$  is the radionuclide distribution coefficient between sediment and water.

Sediment accumulation rates in surface water bodies depend on the size and orography of the catchment area, its geology and pedology, as well as the climatic conditions. Values in the range of 0.1–10 mm/a may give an idea of the order of magnitude involved. When assessing the fate of contaminants in surface water sediments resulting from a singular event, such as an accident, the sedimentation rate will have to be taken into account. It may well be that the contaminated layer becomes buried quite quickly. While burial in deeper sediment layers, which at a later stage often become anoxic, helps to immobilize many radionuclides, these layers constitute a potential second source if disturbed mechanically or chemically.

The accumulating sediments will, over time, undergo compaction and early diagenesis [51]. Owing to its own weight, the sediment becomes increasingly compacted with depth, the excess pore water being expelled to the surface. In consequence, a gradient of downward decreasing porosity develops. The compaction increases the shear strength owing to closer packing of the grains, resulting in a higher erosion resistance. Compaction and early diagenesis are also characterized by various geochemical processes that may either immobilize or release contaminants, depending on the mineralogy of the sediment, its organic matter content and the chemistry of the overlying water, etc. The expulsion of the pore waters may result in a release of dissolved or colloidal contaminants to the overlying surface waters.

### **2.3.5. Filtration**

Sedimentary and colloidal particles to which radionuclides have become bound may be retarded by filtration in porous media. Filtration of particles that are appreciably influenced by surface interaction is a complex process to describe quantitatively [55]. Screening effects will lead to the exclusion of particles, while depth-filtration will result in an effective retardation of particles. Depth-filtration results from the tortuous pathways a particle has to follow through the network of pores in a sediment body. However, these processes are not easy to distinguish in natural sediments as the clogging of pores will eventually result in screening effects.

Colloidal particles that are sufficiently small, together with any associated radionuclides, may diffuse into ‘dead end’ pore spaces or intercrystalline pores in hard rocks and will be physically retarded. The effect will depend on the relative size of the particles and the pore distribution of the host medium, though even small sized colloids may be removed by fine grained clay matrices or fibrous peat.

The assessment of colloid transport requires comprehensive study with respect to permeability, hydraulic conductivity, pore size distribution, heterogeneity, fracture (size) distribution (see Section 2.4.7 on colloid formation).

### **2.3.6. Gaseous transport**

#### *2.3.6.1. Volatilization*

Volatilization is the conversion of a solid or liquid to a gas or vapour by application of heat, reduction in pressure, chemical reaction or by a combination of these processes. Some radionuclides (e.g.  $^{129}\text{I}$ ,  $^{36}\text{Cl}$ ) may be volatilized in the form of organohalides. Chant et al. [56], for instance, highlight the atmospheric dispersion of these isotopes following the Chernobyl accident and their subsequent concentration in lichens (*Parmelia sulcata*). According to Ref. [57], the effect of volatilization and dispersion of iodine is counteracted by pronounced and specific fixation on humic substances after deposition.

Volatile hydride, methylated and permethylated forms of several metals/metalloids (e.g. bismuth, lead, polonium and selenium) are generated microbially in the subsurface; a factor that has yet to be taken into account in safety assessment studies [58]. The process has been known for some time, though only with the advent of modern mass spectrometric techniques has accurate identification and measurement been possible. Those radionuclides showing a tendency for volatilization as organometallic compounds include bismuth, lead, polonium, selenium and tin.

Of particular interest is the microbial mobilization of species incorporated in phases normally regarded as insoluble in ground- or surface waters. Sulphate reducing bacteria acting on baryte or phosphogypsum can promote the release of radium into solution together with polonium and  $^{210}\text{Pb}$  as volatiles [59, 60]. The concentration of sulphide is the key determinant of whether polonium and lead are mobilized or, at higher  $\text{S}^{2-}$  levels, co-precipitated as metal sulphides.

The methylation of polonium has been investigated in both saline and freshwater environments [61, 62]. Under more saline conditions methylcobalamin promoted volatilization but in neither case did any reaction occur when biological activity ceased. These findings suggest that biological mediation is a widespread phenomenon affecting the transfer of polonium to the gaseous phase.

#### 2.3.6.2. *Gas migration*

As a noble gas, radon produced by decay of parent radium isotopes will escape from well-ventilated soils or residues leading to a dispersion of its progeny ( $^{210}\text{Pb}$ ,  $^{210}\text{Po}$ ). This obviously needs to be taken into account when discussing natural attenuation at uranium or radium contaminated sites. The literature describing radon transport in soils [63] and accumulation in buildings or underground workings is very extensive and details need not be provided here. A recent paper dealing with radon emanation from uranium mill tailings [64] describes a simple 1-D model of transport through the unsaturated zone and serves as an introduction to the interested reader.

#### 2.3.6.3. *Airborne particulates*

The atmosphere can provide for rapid dispersal and deposition of radionuclides over long distances away from a release point. As in the case of aqueous media, the transport of radionuclides in the atmosphere is effected by advection, aerodynamic dispersion and diffusion that occur on local and global scales [44, 45]. Once a contaminant is released, dilution and mixing are induced by turbulent eddies and wind shear. In the vertical dimension, these eddies are limited in size by atmospheric mixing layers, whereas in the horizontal dimension, they extend up to the scale of large weather systems.

The advective component can be determined by wind speed measurement and the monitoring of air masses as part of local, regional or global scale weather monitoring networks. Meteorological offices routinely use such data in forecast models to analyse wind fields over a region and to forecast future development.

The greatest risk is associated with submicrometre-sized particles since these can be subsequently inhaled and cause damage to the lungs. Particulates are removed from the atmosphere by two principal mechanisms: wet and dry deposition.

Wet deposition is the removal of particulates from the atmosphere by various types of precipitation. The process involves the dissolution of gases or the incorporation of particles within raindrops and the subsequent deposition of the drops onto the ground or the vegetation. The removal of radioactive particles from the atmosphere by wet deposition depends on complex physical and chemical processes that are a function of both the conditions within and outside the cloud bearing layers of the atmosphere. These processes include nucleation scavenging, particle diffusion to cloud and rain droplets, aerodynamic and electrostatic capture, thermophoresis and diffusiophoresis [45].

The rate of wet deposition  $D$  can be estimated according to the following equation [44]:

$$D = \lambda hCR = v_w C \quad (10)$$

where  $R$  is rainfall rate;  $h$  the thickness of the contaminated layer;  $C$  the average concentration in the air;  $\lambda$  the wash-out coefficient, which is of the order of 0.1;  $v_w$  the wet deposition velocity, which is in the range 1–20 cm/s.

Removal from the atmosphere by dry deposition is important within the atmospheric surface layer where the airborne radioactivity may come in contact with the ground or vegetation by a variety of mechanisms that include diffusion, gravitational settling, impaction, interception, electrostatic effects, diffusiophoresis and thermophoresis. The rate of dry deposition depends on the product of the atmospheric concentration and a so-called deposition velocity  $v_d$ . Many particles have a  $v_d$  in the range 0.01–0.1 cm/s, compared with 0.1–1 cm/s for reactive gases [44]. Deposition rates also depend on the stability of the air mass and the nature of the surface (bare, vegetation, etc.).

Resuspension is the process by which previously deposited material becomes entrained in the atmosphere. Particles may be resuspended as a result of the direct shearing action of the wind or indirectly by the shaking of plant leaves on which particles may have been deposited. It is clear that resuspension is most likely to occur in dry windy conditions; wet conditions increase the surface adhesion, for instance owing to capillary forces between the particle and the surface. Generally, the magnitude of resuspension is difficult to predict [44].

To describe resuspension quantitatively, the term resuspension factor  $R_F$  was introduced, which is the ratio of the airborne concentration (Bq/m<sup>3</sup>) to the material on the surface (Bq/m<sup>2</sup>). For instance at the Chernobyl site  $R_F$  was estimated for particles less than 10  $\mu\text{m}$  diameter and for those greater than 15  $\mu\text{m}$  [65]. The smaller particles had  $R_F$  values of around  $2 \times 10^{-10} \text{ m}^{-1}$ , whereas the larger ones had values ranging from  $2 \times 10^{-10}$  to  $1.7 \times 10^{-9} \text{ m}^{-1}$ , depending on the location. Estimations of the resuspension rate,  $R_R$ , that is, the fraction of the surface deposited activity resuspended per second, in general have a great degree of uncertainty, ranging from  $5 \times 10^{-12}$  to  $5 \times 10^{-10} \text{ s}^{-1}$  for  $^{137}\text{Cs}$ .

Forest and bush fires may also cause large quantities of material to become airborne. For instance, a fire in the 30 km exclusion zone around the Chernobyl plant in 1992 caused the airborne concentration of  $^{137}\text{Cs}$  to increase tenfold to 2.1 mBq/m<sup>3</sup>. About 5% of the deposited material was released during the three-day fire, mainly from the leaf litter which had an effective  $R_R$  of  $10^{-7} \text{ s}^{-1}$ .

#### 2.3.6.4. Modelling airborne transport

The simplest airborne transport model is the Gaussian plume model, which requires only the wind speed and direction at the release location along with estimates of both atmospheric stability and the source term [46, 47]. For a continuous release from an elevated point source under constant wind velocity and atmospheric conditions the Gaussian plume model [47] may be represented by:

$$C_A(x, y, z) = \frac{Q_i}{2\pi\sigma_y\sigma_z} \exp\left(-\frac{y^2}{2\sigma_y^2}\right) \times \left\{ \exp\left[-\frac{(z-H)^2}{2\sigma_z^2}\right] + \exp\left[-\frac{(z+H)^2}{2\sigma_z^2}\right] \right\} \quad (11)$$

where  $C_A(x, y, z)$  is the air concentration ( $\text{Bq/m}^3$ ) at a point  $(x, y, z)$  downwind of the release;  $x$  is the downwind distance (m);  $y$  is the crosswind distance (m);  $z$  is the height above ground (m);  $Q_i$  is the release rate for radionuclide  $i$  ( $\text{Bq/s}$ );  $\sigma_y, \sigma_z$  are the dispersion parameters (m) that are a function of downwind distance  $x$  and atmospheric stability;  $u$  is the mean wind speed (m/s); and  $H$  is the effective height of release above ground (m).

In fact, the value of  $H$  is the physical stack height of the release point plus an allowance for any additional plume rise owing to momentum (e.g. from fan driven exhausts) or buoyancy (e.g. from hot flue gases). The effective stack height depends on atmospheric conditions and may be higher for quiet weather than for windy conditions in which case it would be closer to the physical stack height.

The dispersion parameters incorporate the basic assumption of the model whereby a plume spreads both laterally and vertically with a Gaussian distribution. The form of the model represented by Eq. (11) includes reflection of the plume at ground level. In theory, the Gaussian plume model is limited to rather simple dispersion situations [47]; however, in practice it has been successfully applied to a wide variety of dispersion problems.

Over long distances, modelling may require trajectory analysis. The simplest long range dispersion models merely involve assuming a plume extending along the estimated trajectory, similar to an extended version of the Gaussian plume model used at shorter distances. The models presented are designed for use with releases from point sources, not area or volume sources such as uranium mill tailings. It has been suggested, however, that the following

procedures could be used to calculate the concentration in air from an area source [47]:

- (a) Calculate a pseudo-point source release rate by integrating over the entire area of the source;
- (b) Assume the release height to be zero;
- (c) Locate the release point at the edge of the area source nearest the location of concern.

Use of this procedure should result in a conservative estimate of the concentration in air [47]. What is to be considered a point source and what would be an extended source also depends on the size of the source relative to the size of the domain over which transport is to be modelled.

## 2.4. CHEMICAL PROCESSES

### 2.4.1. Introduction

Speciation refers to the different chemical forms of an element that together make up its total concentration in solution. Simple inorganic ions in aqueous media often react with other ions present to produce stable ion pairs or more complex molecules. These species, in turn, influence interaction with mineral surfaces, bioavailability and the tendency to form solid compounds. The reactions are amenable to treatment using thermodynamically based numerical models and such tools are now used routinely in groundwater protection to predict the sensitivity of aquifer systems to environmental perturbations. For a summary of the current status the reader is referred to one of several excellent textbooks on the subject [66, 67].

### 2.4.2. Aqueous complexation

Approaches to modelling aqueous speciation entail minimizing the Gibbs free energy of a system at equilibrium, either directly [68] or indirectly [69]. The latter is far more common; thus, for the general reaction:



A formation constant,  $\beta$ , is defined as:

$$\beta = \frac{[P_a Q_b^{ax-by}]_{(aq)}}{[P^{x+}]^a [Q^{y-}]^b} \quad (13)$$

where  $x$  and  $y$  are the ionic charges,  $a$  and  $b$  stoichiometric reaction coefficients and the square brackets denote activities.

In any closed system, a mass balance may be written for each chemical component. Therefore, by substituting mass action expressions of the type shown above into the mass balance terms and solving the resulting equations numerically the minimum Gibbs free energy condition, corresponding to system equilibrium, may be calculated.

Each of the equilibrium speciation models described in Section 5.1 employ a thermodynamic database comprising formation constants of this type. In recent years many such databases have been compiled, each differing from the next depending on perceived requirements, alternative methods of data manipulation and the compiler's judgement [70]. Often, the selections were based on earlier compilations by other workers, with the result that errors were propagated. An example in the case of uranium chemistry is described below.

The following sections, summarizing current knowledge of the aqueous geochemistry of some relevant radionuclides, draw heavily on the findings of the OECD Nuclear Energy Agency's (OECD/NEA) thermodynamic database (TDB) [71], since this source is indispensable in the present context. The situation with respect to mineral solids is rather different, as discussed further in Section 2.4.4.

### 2.4.3. Complexation by natural organic matter

A number of radionuclides exhibit significant migration potential in the presence of aqueous, low molecular weight organic compounds [72, 73]. Equally, however, immobile organic matter in the form of peat [74–76] or organic-rich horizons in soils and sediments may provide an excellent substrate [74, 77] for radionuclide retention. These phenomena have been studied extensively in the context of 'natural analogue' studies used in the performance assessment of radioactive waste repositories [38, 39, 78, 79]. Uranium concentrations approaching percentage levels have been reported in peat from Canada and northern Europe, whereas iodine, often considered to be a conservative tracer in such assessments, has been shown to be fixed in organic-rich lacustrine deposits [80].



#### 2.4.4. Precipitation and dissolution

This section and the next address heterogeneous reactions rather than those occurring exclusively in solution. As with aqueous chemistry, the focus is on equilibrium approaches, given the comparative lack of rate constants. However, heterogeneous reactions are generally much slower than those in solution and so examples are given of non-equilibrium behaviour where data allow.

Precipitation and co-precipitation are the most significant processes leading to the fixation of trace elements in rocks and soils. The converse process of dissolution is the key to determining source terms for contaminants. They can be represented by mass action expressions analogous to those for aqueous complexes:



$$K_{sp} = [P^{x+}]^c [Q^{y-}]^d \quad (15)$$

where  $c$  and  $d$  are stoichiometric coefficients and  $K_{sp}$  is the solubility product of solid  $S$ .

Dissolution is often a slow process and one controlled by the surface layer exposed to solution. Release of trace components is difficult to predict but congruency with the dominant ions present cannot be assumed. Weathering of uranium and thorium ores invariably leads to fractionation. Oxidation of uranium and complexation of the uranyl ion in solution results in greater mobility and transport further from the source [81, 82]. The rare earth elements, which are predominantly trivalent, display enhanced mobility relative to thorium but tend to be less easily transported than uranium [83]. These observations may provide some insight into the likely fate of the trivalent transuranics, such as americium or curium.

Very few natural minerals display their ideal stoichiometric composition owing to lattice substitution. The resulting solid solutions may be homogeneous but, more commonly, substitution leads to structural rearrangement and zoning [84]. Several theoretical approaches to the treatment of dissolution/precipitation of solid solutions have been developed. These differ in the method used to account for the activity composition relationship in the solid phase.

Relatively few natural series radionuclides and no artificial isotopes will exist in sufficient mass concentrations to precipitate as a pure phase from ground-, surface or pore waters. The exceptions are uranium, lead and thorium. Radionuclides present at very low mass concentrations can nevertheless form solid phases by co-precipitation in mineral lattices. An important example from

both a nuclear and NORM perspective is the high selectivity shown by radium for baryte, a system that has been very well characterized [85] and is also exploited in a remediation context [86, 87]. It is likely that transuranic isotopes would be similarly incorporated in uranium- and lanthanide-bearing minerals. There is evidence that this would be the case from extensive laboratory studies [88], though it remains to be confirmed in the field. Establishing the geochemical controls on migration of artificial radionuclides represents the major challenge to workers involved in remediation of legacy nuclear sites.

Co-precipitation on ferric oxyhydroxide flocs is an extremely efficient removal mechanism for a large number of radionuclides in solution. As the contaminants tend to be released upon crystallization to goethite, the process is often classified under the more general heading ‘sorption’.

At its simplest and in the absence of further information, the activity of an end member component is often assumed to be proportional to its respective mole fraction [89]. However, this assumption has little experimental basis. The degree of equilibrium attained during solid solution–aqueous solution reactions determines the composition of the solids formed during precipitation and the final composition of the aqueous phase. If diffusion is effective throughout the solid phase and full equilibrium is maintained, compositionally homogeneous crystals may form. This is termed Berthelot–Nernst precipitation [90] and represents one end of the spectrum. If, on the other hand diffusion in the solid phase is slow, the interior of a crystal will lose contact with its surface and the aqueous phase leading to compositionally zoned crystals. A commonly used convention to account for the latter type of behaviour is the Doerner–Hoskins Law, originally derived for the radium–barium sulphate system [91].

In practice, the precipitation process is more complex and highly parameterized models are needed to account for the evolving solid and liquid phases. Lippmann [92] introduced the concept of the ‘total solubility product’ variable,  $\Sigma\pi$ , given by:

$$\Sigma\pi = K_{BA}X_{BA}\gamma_{BA} + K_{CA}X_{CA}\gamma_{CA} \quad (16)$$

where  $K_{BA}$  and  $K_{CA}$  are the solubility products of pure end member phases, BA and CA,  $X_{BA}$  and  $X_{CA}$  are the corresponding molar fractions in the solid solution and  $\gamma_{BA}$ ,  $\gamma_{CA}$  are the activity coefficients of the two components in the solid phase. Thus, the total or overall solubility product is not a constant but a function of the solid solution composition (solidus relation). It is also a function

of the aqueous solution composition, which changes in response to the solid (solutus relation):

$$\Sigma\Pi = \frac{1}{\frac{X_{B,aq}}{K_{BA}\gamma_{BA}} + \frac{X_{C,aq}}{K_{CA}\gamma_{CA}}} \quad (17)$$

$$X_{B,aq} = \frac{[B^+]}{[B^+] + [C^+]} = \frac{\gamma_B^+ m_B^+}{\gamma_B^+ m_B^+ + \gamma_C^+ m_C^+} \quad (18)$$

$$X_{C,aq} = \frac{[C^+]}{[C^+] + [B^+]} = \frac{\gamma_C^+ m_C^+}{\gamma_C^+ m_C^+ + \gamma_B^+ m_B^+} \quad (19)$$

where  $\gamma_B^+$ ,  $\gamma_C^+$  are the activities and  $m_B^+$ ,  $m_C^+$  the molalities of the aqueous ions, respectively.

Solidus and solutus curves can be plotted to predict the solubility of any binary solid solution and tie lines used to obtain the solid and aqueous phase compositions for any given equilibrium state.

Further refinements to the above modelling approach can be introduced to reflect the fact that formation of solid solutions often occurs at supersaturation rather than equilibrium. A paper by Putnis and co-workers describes the current state of the art [93]. Ceccarello et al. [94] discuss recent data for radium incorporation in baryte scale.

## 2.4.5. Sorption

### 2.4.5.1. Introduction

Adsorption is the net accumulation of matter at the interface between a solid phase and an aqueous solution [95]. It may be brought about in several ways ranging from relatively weak van der Waal's attraction to specific chemical bonding between the aqueous species and functional groups on the surface. The former is easily reversible, whereas the latter often displays hysteresis owing to slow desorption kinetics. Both depend on the availability of surface sites and, hence, are a function of grain size, mineralogy and the solid:solution ratio. Chemical bonding, which results in structural rearrangement of the surface, is considered the first step in the formation of a

discrete solid phase. It is without doubt an important though transient process in the sequestration of aqueous ions in natural waters.

The related term ‘sorption’ has been employed somewhat loosely in the field of radioactive waste management to describe almost any form of trace element partitioning between solution, usually groundwater, and a solid surface. Idealized reversible equilibrium is typically assumed. When used in this way, it is taken to encompass not only surface adsorption in the strict sense, but processes more accurately described as co-precipitation since they are not confined to the mineral surface. This has led to confusion in the past and to misinterpretation of field and laboratory data. Precipitation processes are dealt with separately in Section 2.4.4 as the latter clearly extends beyond the surface, resulting in the formation of a defined mineral phase [96].

Clay minerals typically show a strong affinity for radionuclides in the cationic form [97–100]. Geological media with high clay mineral contents are more likely, therefore, to effect attenuation. Adsorption and ion exchange would be expected to play an important role in retarding the migration of soluble mono- and divalent ions. Examples include the pronounced retention of caesium on zeolites (e.g. clinoptilolite [101]) and the substitution of strontium for interlayer cations in smectites [102, 103]. For multivalent ions surface sorption is an important transient in the formation of new mineral phases [104, 105].

#### 2.4.5.2. *Empirical approaches to surface adsorption*

Several models have been used to describe surface adsorption. The simplest are empirical and use experimentally derived ‘equilibrium coefficients’ to account for the partitioning between solid and solution. Since the experiments are usually performed at constant temperature, these models are termed ‘isotherms’. The most commonly used are the Freundlich [106] and Langmuir [107] isotherms, though many others exist, for example the Redlich–Peterson and Dubinin–Radushkevich [108] isotherms. The Freundlich isotherm is given by:

$$C_{\text{sorb}} = K[C_{\text{sol}}]^n \quad (20)$$

where  $C_{\text{sorb}}$  is the sorbed concentration,  $C_{\text{sol}}$  is the concentration in solution, and  $K$  and  $n$  are constants. The latter constant ( $n$ ) is obtained from a plot of  $\log C_{\text{sorb}}$  against  $\log C_{\text{sol}}$  and normally has a value below unity. When  $n$  is unity, the above equation reduces to that for linear, reversible sorption with  $K$  becoming the distribution coefficient,  $K_d$ .

The Langmuir isotherm also has two adjustable parameters and is given by:

$$C_{\text{sorb}} = \frac{KC_{\text{sol}}M}{(1 + KC_{\text{sol}})} \quad (21)$$

where  $M$  is the maximum amount of solute adsorbed, or sorption capacity. When  $C_{\text{sol}}$  is small and  $KC_{\text{sol}}$  is  $\ll 1$ , then the equation reduces to that for linear, reversible sorption with  $KM$  again becoming the distribution coefficient,  $K_d$ .

The appeal of these relationships lies in their simplicity, the ease of generating experimental data from batch experiments and the wealth of empirical measurements in the literature. An evaluation of the data requirements of different isotherm models and their application in radioactive waste disposal has been made by Kinniburgh [109].

$K_d$  values are widely used in experimental evaluations and in performance assessment for radioactive waste repositories in spite of their limited theoretical foundation. Most nuclear waste disposal agencies have a database of  $K_d$  values, which they draw on for safety calculations. Several were compared by McKinley and Scholtis [110], who found large differences in the constituent data and supporting documentation. More recent reviews suggest that the situation has changed relatively little in the intervening years [111, 112].

Critics of empirical isotherm models focus on the underlying assumptions, principally:

- (a) They take no account of aqueous chemistry;
- (b) The solute behaves ideally in solution and the process of solute uptake has no effect on the solid phase;
- (c) Adsorption and desorption are equally rapid such that instantaneous, reversible equilibrium is maintained;
- (d) There is no competition for surface sites.

Perhaps the main shortcoming, however, is that for many elements the models do not represent the processes actually occurring. For example, a Freundlich isotherm or even a constant  $K_d$  model may be sufficient to account for uptake of caesium on kaolinite but would be less successful if applied to more highly charged or complexed aqueous species.

As with many types of model, the level of sophistication needed with respect to conceptually representing processes may vary with the scales of space and time. The  $K_d$  concept may well be applicable to large scale models of low spatial resolution.

#### 2.4.5.3. Mechanistic approaches to surface adsorption

Surface complexation models were developed in order to characterize adsorption at amphoteric surfaces in terms of chemical and electrostatic interactions. Many minerals contain functional groups on the surface that acquire an electrical charge, depending on the redistribution of aqueous species in the interfacial region [95, 113]. They include the clays, with silanol and alumina groups, and oxides/hydroxides. In these models, the adsorbed ions are assumed to be positioned at one or more planes. The number of planes varies according to the model but the basic principles are the same [95]:

- (a) There are specific sites on the surface where adsorption reactions take place;
- (b) These reactions can be described quantitatively, via mass action laws;
- (c) The charge on the surface results from adsorption/desorption reactions;
- (d) The activities of the sorbed ions include a contribution relating to the potential of the adsorbing plane.

Thus, for deprotonation of a surface site:



The reaction is written as:

$$K = \{SOH\}\{H_s^+\}/\{SOH_2^+\} \quad (23)$$

where the subscript s indicates the species located at the surface, K is the equilibrium constant and {} denotes activity at the surface.

The activity of a surface species can be related to its activity in the bulk solution by considering the electrostatic work involved in transporting ions through the interfacial potential gradient:

$$\{H_s^+\} = \{H^+\} \exp(-e\psi/K_b T) \quad (24)$$

where  $e$  is the electronic charge,  $\psi$  is the potential at the surface,  $K_b$  is the Boltzmann constant, and  $T$  is the absolute temperature.

If it is assumed that surface species have the same activity–concentration relationship, then

$$K = ([SOH]\{H^+\}/[SOH_2^+]) \exp(-e\psi/K_b T) \quad (25)$$

Several such models have been developed, the most commonly used being the constant capacitance [114], diffuse double layer [115], triple layer [116] and non-electrostatic models [117]. Briefly, the constant capacitance model assumes that all of the adsorbed ions are attached to a single plane and are at the same potential. The surface potential is taken to be linearly related to the surface charge:

$$\sigma = C\psi \quad (26)$$

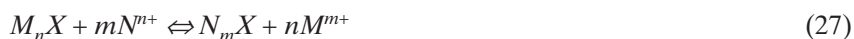
where  $\sigma$  is the charge and  $C$  the capacitance.

The diffuse double layer and triple layer models relate surface potential to charge via the Gouy-Chapman description of Helmholtz planes and invoke a larger number of adjustable parameters. The latter include the specific surface area of the adsorbent, the capacitances of the surface layers, the concentration of available sites and a set of constants for the surface reactions (protonation and deprotonation of the surface as a function of pH, adsorption of background electrolyte ions and the ions of interest, etc.). This may account in part for their greater success in reproducing experimental data. For further details the reader is referred to Dzombak and Morel [95].

Although they represent a significant advance on the empirical approaches described previously, surface complexation models have their limitations. The constant capacitance model, for example, takes no account of the ionic strength of the solution. The double and triple layer models do account for such factors but imply in-depth knowledge of the attachment mechanism at the surface, a level of detail that is difficult to obtain directly from experiment and often out of scope in field cases.

#### 2.4.5.4. Ion exchange

Ion exchange is also often included under the heading ‘sorption’. At its most general, it involves the replacement of one ionic species in a solid phase by another taken from solution. For an exchange between cations  $M$  and  $N$  this can be represented by the equation:



The process may take place at the mineral surface or, in the case of some phyllosilicates (e.g. swelling clays), by replacement of interlayer ions. Only fully solvated ions bound via outer sphere complex or diffuse ion swarm mechanisms are readily exchangeable such that ion exchange as usually defined is a non-specific, reversible, adsorption process involving electrostatic bonding.

The most important phases for ion exchange reactions are the clay minerals and zeolites, which tend to have permanently charged surfaces and significant cation exchange capacities. In alkaline soils the readily exchangeable cations are  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^{+}$  and  $\text{K}^{+}$ . In acidic soils the most important exchangeable cation is  $\text{Al}^{3+}$ , followed by  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Ion exchange for high valence radionuclides appears to be much less significant owing to size–charge considerations and ease of hydrolysis. However, the alkali and alkali earth ions are readily bound by montmorillonite. The potential retardation of  $^{137}\text{Cs}^{+}$  and  $^{90}\text{Sr}^{2+}$  accounts for the popularity of bentonite as a candidate backfill for repositories.

#### **2.4.6. Isotopic substitution**

Another, possibly minor, mechanism that can lead to a reduction of a radioactive contaminant in the aqueous phase is isotopic substitution. This phenomenon is based on dissolution/precipitation or desorption/sorption processes where an inactive compound is dissolved or a non-radioactive isotope is desorbed. At a later precipitation or sorption stage the isotopes are built into the solid or sorbed according to their isotopic ratio in the solution, which has now been isotopically diluted by the inactive isotopes. Both the heterogeneous reaction and the dilution lead to an attenuation of the dissolved concentration of the radioisotope.

#### **2.4.7. Colloid formation**

Colloids are a specific form of solid matter in aqueous solution in which particle interactions prevent sedimentation. Colloids can form as the result of mechanical dispersion of solids (rock fragments, sediment grains, bacteria, etc.) or by precipitation from solution. The behaviour and stability of colloidal solutions is controlled mainly by pH and ionic strength. Both parameters control the surface charge and diffuse layer around the suspended particulates, hence their interaction. Increases in the ionic strength or a decrease in the pH of the media will reduce the surface charge and consequently the intensity of particle interaction. McCarthy and Zachara [118] describe three main steps in mobile colloid formation. The first step involves the formation of a colloidal suspension in pore water. In the second step, the colloids must become stabilized in the groundwater. In the third step, the stable colloid will either be transported or filtered.

There are different types of colloid that can be seen in groundwater, some of these are summarized as follows [119, 120]:



- (a) Mineral fragments are generally hydrophobic, hard particles that are kinetically stabilized by electrostatic forces and many consist of crystalline or amorphous solids. Mineral fragments may act as substrates for sorption of radionuclides. They may also consist of precipitated or co-precipitated actinide solids.
- (b) Humic substances are generally hydrophilic particles that are stabilized by solvation forces. They can be powerful substrates for uptake of metal cations and are relatively small (less than 100 000 atomic mass units).
- (c) Microbes are relatively large colloidal particles that are stabilized by hydrophilic coatings on their surfaces that behave as steric stabilizing compounds. They may act as substrates for extracellular actinide sorption, or they may actively bioaccumulate radionuclides intercellularly.

Colloid stability and concentration are very important factors relating to colloid transport. In order for radionuclide-bearing colloids to affect radionuclide transport, the colloidal dispersion must be stable for the time-frame of transport and must carry significant amounts of radionuclides. Transport times can range from days to years or hundreds of thousands of years for retarded transport to the accessible environment. The more stable colloids, however, may remain suspended for years and travel a much greater distance [121].

The stability and the coagulation, or agglomeration, of colloids are controlled by electrostatic and chemical processes at the colloid surfaces. Hydrophobic colloidal particles are kinetically stabilized and destabilized by electrostatic forces. Mineral fragments, which are a hydrophobic colloid type, are affected by ionic strength in this way. Hydrophilic colloidal particles are stabilized by solvation forces, which are largely independent of the ionic strength of the dispersant. This type of colloidal particle is essentially a dissolved macromolecule. Humic material is an example of the traditional hydrophilic colloid type.

## 2.5. BIOLOGICAL PROCESSES

### 2.5.1. Overview

The affect of organisms on the fate of contaminants in soils can be direct and indirect. Biological activity in a soil system is strongly affected by the soil's physical and chemical characteristics, including acidity, redox potential, nutrient availability, pore space availability, etc. In turn, biological activity

changes the physical and chemical characteristics of the environment, and then is able to affect, indirectly, contaminant speciation and mobility.

The role of metalloids as a substrate on which to grow microorganisms is gradually being considered: bacteria contribute actively to the cycles of iron, uranium, arsenic, selenium, etc. Microorganisms can utilize redox reactions of metals or metalloids in their energetic metabolism. Thus, metabolic activity can result in the direct reduction or oxidation of contaminants. It can also lead to contaminant accumulation in a biological matrix, complexation by organic ligands (intra- or extracellular), methylation and volatilization (see Section 2.3.6.1). Biological processes can enhance the retention of radionuclides in a soil or a sediment but the sustainability, efficiency and duration of these processes depends on many parameters, such as the presence and diversity of micro- or macroorganisms, the toxicity level of the contamination to these organisms, nutrient availability, and the bulk chemical conditions in the medium (especially redox and pH). These parameters are sometimes difficult to estimate in the context of the envisaged long term natural attenuation processes.

## **2.5.2. Biologically induced physical changes**

Macrobiota, such as plants and macrofauna, affect the soil texture and porosity distribution by creating preferential water flow pathways along (decayed) roots and through bioturbation by worms or by other burrowing invertebrates and vertebrates. These processes lead to a heterogeneous distribution of permeability, but in the case of extensive bioturbation also to a mixing and homogenization over the longer term. Therefore, these processes may change the hydrodynamic properties of the geological media over time and cause the dispersion of the contaminants.

The physical process of bioturbation and the ensuing mixing of soils will also affect the redox state of soils and stream and lake sediments. Namely, bioturbation may introduce oxygen into the affected layers.

## **2.5.3. Biologically induced chemical changes**

### *2.5.3.1. Metabolic effects*

Living cells extract their energy and matter from their environment for metabolic, growth and reproductive purposes. Energy gain involves the transfer of electrons from an electron donor to an electron acceptor. Electron donors and terminal acceptors can be inorganic as well as organic components. Together with the energy source (carbon), they define the trophic status of the

TABLE 3. MAJOR TROPHIC STATUS OF LIVING ORGANISMS

		Electron donor	
		Mineral phase	Organic matter
Energy source	Light	Photo-lithotrophy	Photo-organotrophy
	Chemical reaction	Chemo-lithotrophy	Chemo-organotrophy

living organisms (Table 3). The chemo-lithotrophic and chemo-organotrophic bacteria are directly involved in the increase in solubility of metals, metalloids, radionuclides, etc., due to strongly complexing components and by modifying pH and redox conditions (e.g. oxidation or reduction of iron, manganese and sulphur) [122].

Table 4 highlights the possible effects of the metabolism of living organisms on the chemical properties of soils and groundwaters. For instance, photosynthesis leads to an increase in the redox potential (O<sub>2</sub> production),

TABLE 4. SOME METABOLIC MECHANISMS OF MAJOR INTEREST IN SOILS

Trophic status	Electron donor	Electron acceptor	Metabolic by-products	Metabolic mechanism
Photo-lithotrophy	H <sub>2</sub> O	CO <sub>2</sub>	O <sub>2</sub>	Photosynthesis (e.g. plants, cyanobacteria)
Chemico-organotrophy	Organic compound	Organic compound	Lactate, acetate	Fermentation (e.g. yeasts in anaerobic conditions)
	Organic compound	O <sub>2</sub>	CO <sub>2</sub>	Aerobic respiration
	Organic compound	Inorganic compound other than O <sub>2</sub> , e.g. SO <sub>4</sub> <sup>2-</sup> , Fe(III), NO <sub>3</sub> <sup>-</sup>	CO <sub>2</sub> , HS <sup>-</sup> , Fe(II), NH <sub>4</sub> <sup>+</sup>	Anaerobic respiration (e.g. sulphate reducing bacteria)

whereas fermentation and aerobic and anaerobic respiration lead to a decrease of this potential (e.g.  $O_2$  consumption or release of organic acids or  $HS^-$ ). By producing  $CO_2$ , respiration processes acidify the environment surrounding an organism. These changes can affect the speciation of the contaminants in the vicinity of the biologically active zone, especially the redox speciation (Fig. 3) [123]. In addition, fulvic and humic acids are partly the result of the biological activity in soils. Biological activity also directly affects complexation capacity, exchange capacity and colloid mediated transport in soils.

Anaerobic bacteria in the subsurface are able to respire on a variety of terminal electron acceptors (e.g.  $NO_3^-$ , Fe(III),  $SO_4^{2-}$ ,  $Mn^{2+}$  [124]), including trace

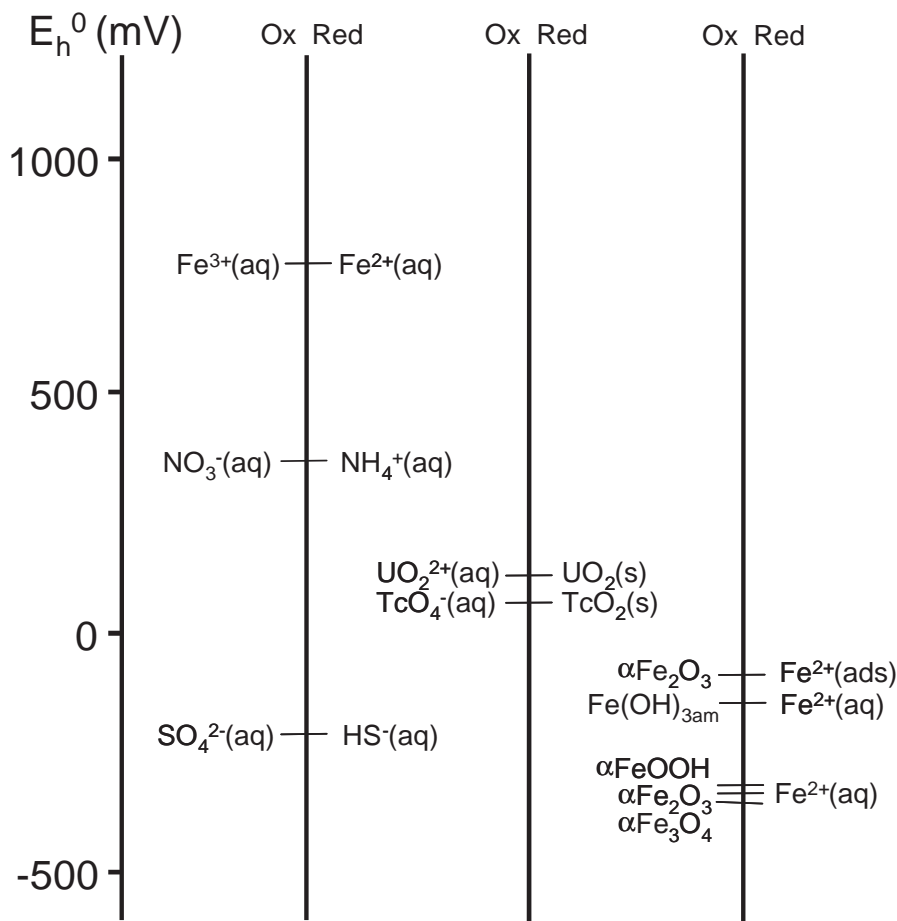


FIG. 3. Redox potential of selected radionuclides compared with standard redox potentials of major biological reactive by-products. Modified after Charlet et al. [123].

metals such as U(VI) [125], Tc(VII) [126] and possibly Pu(V) or Pu(VI) [127], leading to the production of insoluble species, such as  $\text{UO}_{2(s)}$ , and to a following decrease of contaminant mobility. Since bacteria respiration processes occur on their cell membrane, the respiration processes involving xenobiotic compounds could take place either on the outside of the cell membrane or within it; for instance, U(VI) is brought into the periplasm, where it is reduced to  $\text{UO}_{2(s)}$  and then secreted from the cell [128].

More complicated schemes involving biologically enhanced inorganic processes can also take place in a biologically perturbed area. For instance, Liger et al. [129] have shown that U(VI) is efficiently reduced by Fe(II) sorbed onto haematite surfaces. Reduction processes in a multiple step mechanism are likely to occur, including biological Fe(III) oxyhydroxide reductive dissolution, followed by Fe(II) readsorption on the solid and heterogeneous catalysis of redox reaction at the solid–water interface [130]. Beyenal et al. [131] suggest that sulphate reducing bacteria immobilize uranium both enzymatically (likely with cytochrome implicated [132, 133]) and chemically (by reaction with microbially generated  $\text{H}_2\text{S}$ ).

#### 2.5.3.2. Biosorption, biotransformation and bioaccumulation

Metals are bound to living or dead cells by the same mechanisms as those causing sorption on inorganic compounds, e.g. Van der Waal's and electrostatic interactions. Cell walls and membranes are likely to sorb metals owing to the presence of carboxyl, phosphoryl and amine functional groups on polysaccharides, lipids and proteins. See, for instance, Refs [128, 134] for uptake on bacteria, Ref. [135] for uptake on the yeast *Saccharomyces cerevisiae* and Ref. [136] for uptake by algal and fungal biomasses.

The  $\text{UO}_2^{2+}$  ion can be complexed with functional groups, such as phosphate and carboxyl groups, on bacterial walls. It has been shown that uranium is significantly sorbed onto *Shewanella putrefaciens*, an anaerobic Gram negative bacterium, in the 2–8 pH interval [128]. Since the bacterial uranium uptake is reversible by decreasing the pH, the uptake phenomenon is likely to be due to adsorption and not to incorporation into the cell or to other metabolic activity. In aerobic media, Gram positive bacteria, such as *Bacillus sp.*, are also able to sorb U(VI) on their cell wall [134].

Several studies have shown the biosorption of thorium ( $\text{Th}^{4+}$ ) onto fungal biomasses, such as *Rhizopus arrhizus* and *Aspergillus niger* [137, 138]. In this way bacteria contribute directly to the cation exchange and sorption capacity of soils.

The biosorption of contaminants on cell membranes can also result in an accumulation in the colloidal organic fractions that can drag these elements

towards the bottom. This mechanism was observed for plutonium at different US and German sites [122].

Bioaccumulation concerns only the living cell because this mechanism involves passive diffusion and active transport into the cell. Sometimes, bioaccumulation leads to the precipitation of metals inside the cell. This has been observed for several elements, e.g. lanthanum, uranium and thorium [139]. The accumulation of uranium is notable in some microorganisms such as *Aspergillus ochraceus* [140] and *Mycobacterium smegmatis* [141].

In the cell, toxic metals and radionuclides may be sequestered by cysteine metallothioneins [142] and in fungi, compartmentalized into the vacuole [138]. Investigations performed on cell thin sections have shown  $\text{UO}_2^+$  accumulation on the inner and outer membranes of *Citrobacter sp.* and *Pseudomonas sp.* [143, 144], and in the cytoplasm of *Pseudomonas aeruginosa* [145].

Once accumulated on or incorporated into a living cell, contaminants can be degraded or transformed as a result of the cell's metabolic activity. Biodegradation typically only happens to organic contaminants and proceeds to some other (smaller) organic compounds or, finally, to inorganic compounds such as  $\text{CH}_4$  or  $\text{CO}_2$ . Metals and radionuclides cannot be biodegraded, but their speciation and subsequent mobility can be drastically altered through the action of living organisms. However, bioaccumulation (e.g. in plants and mushrooms) can have the unwanted effect of generating secondary sources for migration and can also result in exposure when consumed.

Examples of anaerobic respiration involving U(VI) and subsequent precipitation as U(IV) were given in Section 2.5.3.1. Uranium(IV) is likely to be secreted by the cell in a solid form which then accumulates outside the cell. The microorganisms catalyse the transformation by enzymatic complexes. Amachi et al. [146, 147] demonstrated the capability of bacteria to promote the formation of methyl iodine ( $\text{CH}_3\text{I}$ ) in aerobic conditions, thus effecting the removal of iodine from soils.

The biomethylation of radionuclides has received little attention. This is mainly due to the instability of the methylated compounds. Some microorganisms can act directly on the elements by oxidation or reduction or by methylation processes. The element concerned can be either the donor or acceptor of electrons.

Some plants are able to concentrate contaminants in their tissues. In most cases, the plants develop a mechanism of physiological tolerance to toxic elements. In the presence of high concentrations of toxic elements, these plants produce a wide variety of compounds that complex these elements, such as amino acids, citric acid, maleic acid and proteins. The phytochelatin is the main molecule involved in the decrease of metal toxicity in the cytoplasm and the accumulation of metals in the plant cell [148]. Some plants, dubbed 'hyper-

accumulator' plants, are capable of accumulating certain contaminants to levels exceeding 1% of their dry weight, and are thus able to resist high contaminant concentrations in their substrate, for instance *Calluna vulgaris* for caesium, *Brassica napus* for selenium and *Thlaspi caerulescens* for lead [122] (refer to Ref. [16] for a discussion on the utilization of these properties for remediation purposes).

#### 2.5.3.3. Biomineralization

Beyond developing physiological resistance [149], microorganisms are able to precipitate metals and radionuclides with microbially generated ligands such as sulphide or phosphate [150]. Biomineralization by microorganisms has been shown for sulphate reducing bacteria, which are able to precipitate metals and radionuclides with sulphide. This mechanism has been tested for the remediation of contaminated soils [151].

Biomineralization, 'biosorption' and microbially mediated phase transfer can therefore effect attenuation. The complex biogeochemical processes effecting fixation or mobilization of metals, including radionuclides, in various types of soil ecosystem have been studied with increased intensity in the aftermath of the Chernobyl accident [152] and in other remediation contexts [153].

### 3. GEOCHEMISTRY OF SELECTED RADIONUCLIDES

#### 3.1. INTRODUCTION

The aim of this Section is to review, for selected natural and anthropogenic radionuclides, current knowledge regarding their aqueous chemistry together with heterogeneous reactions and the nature of solid phases that might control their solubility in near surface environments.

The environmental chemistry of the transuranic elements (neptunium, plutonium, americium, curium, berkelium, californium, einsteinium and the heavier elements) is not very well known. Their occurrence is linked to weapons testing [154], major nuclear accidents [155] and inadequate waste disposal practices [19]. Consequently, our knowledge of their environmental behaviour is limited to the past few decades. Recourse is often made in long term risk assessment to data from chemical analogues [156], for example,

U(IV)/(VI) for Pu(IV)/(VI), or the lanthanides (e.g. neodymium) for the trivalent elements, such as americium and curium. This report highlights the chemistry of neptunium, since it is less amenable to the analogue approach.

The majority of fission products also occur as stable isotopes of elements that are widespread in the environment, e.g. caesium and strontium. As a result, their behaviour in both soils and shallow groundwater systems is reasonably well understood. Focus here is placed on technetium, an artificial element whose chemistry is sufficiently distinct to merit separate treatment. As with the transuranics, our observations of technetium in the environment are restricted to the recent past, in sharp contrast to its future persistence (the half-life of  $^{99}\text{Tc}$  is 213 000 a).

The field of environmental radioactivity has expanded rapidly over the past thirty years, largely in response to concerns surrounding the safety of radioactive waste disposal [157, 158] and of soils following the Chernobyl accident. It is not possible to provide more than a superficial coverage of the vast body of literature available, particularly for uranium and its progeny, in so short a report as this. Even for the less well-studied elements neptunium and technetium, the report does not purport to be exhaustive. Rather, an attempt is made to highlight the principal sources of information that can be accessed by the interested reader. For this reason, all reference material cited is to be found in the open literature and most has been subjected to external peer review. The sources include:

- (a) Documents published by international agencies, for example the OECD/NEA, the European Commission and, of course, the IAEA;
- (b) Technical reports produced within national programmes on radiological protection or waste disposal, mainly in Europe and the United States of America;
- (c) A relatively small number of reports and papers describing industrially sponsored research, provided access to such information is unrestricted.

Finally, since this report focuses on natural attenuation at contaminated sites, planned disposal of radioactive waste in engineered facilities and authorized discharges to marine or freshwater courses are not considered.



## 3.2. GEOCHEMISTRY OF URANIUM

### 3.2.1. Aqueous chemistry

The aqueous chemistry of uranium has been the subject of intensive study owing to the need to understand its behaviour at all stages of the nuclear fuel cycle. Much of the published work, driven first by the Manhattan Project and subsequently by the civil nuclear power industry, is not directly relevant here. For the interested reader, Katz et al. [159] give an excellent overview of the properties of uranium and its compounds, while a more detailed coverage of uranium chemistry is contained in Gmelin's Handbuch [160].

The most stable oxidation state of uranium in aqueous solution is U(VI), where it exists as the uranyl ion,  $\text{UO}_2^{2+}$ . Reduction to U(IV) occurs readily and to U(III) less so. The stability of the pentavalent ion  $\text{UO}_2^+$  has been disputed over the years because of its tendency to disproportionate [161]. In this respect, uranium differs markedly from neptunium for which  $\text{NpO}_2^+$  is the stable form in oxidizing solutions.

Only U(VI) and U(IV) are important in natural waters, where uranium concentrations range from a few parts per billion to several parts per million, depending largely on pH, Eh and carbonate concentration [162, 163]. Ivanovich and Harmon [40] describe the occurrence of uranium and progeny in diverse geochemical environments and set out the basis for uranium series studies into dating and provenance.

Thermodynamic databases designed for environmental modelling applications (e.g. Ref. [164]) invariably contain some entries from the original source literature, some drawn from previous compilations (e.g. Ref. [165]) and several data values obtained by estimation. In recognition of this, Grenthe et al. [161] undertook a thorough review of published formation constants for aqueous uranium species, highlighting inconsistencies as they occurred and arriving at a set of recommended values. Their work helped resolve many ambiguities, for example, those surrounding the relative stability of U(VI) phosphates in natural waters. Moskvina et al. [166] had ascribed greater stability to uranyl complexes with  $\text{HPO}_4^{2-}$  than even to carbonate species. This study was accepted and given added credence by Dongarra and Langmuir [167]. The data were subsequently adopted by numerous thermodynamic data compilers around the world before the stability constants were shown to be erroneous [161]. The implications of these findings for groundwater migration and, hence, safety assessment calculations are profound.

Following the review and recommendations of the OECD/NEA TDB [161–168], the aqueous chemistry of uranium can be predicted with a good degree of confidence. It is known that, once oxidized, uranium is mobile in near

surface waters. Other than hydroxyl, the dominant ligands are carbonate and, in strongly acidic solutions, sulphate [169, 170]. These predictions have been borne out by numerous studies of uranium ore bodies around the world [171]. Indeed, sulphuric acid and alkali carbonates are the favoured methods for chemical leaching in industrial uranium extraction [172, 173].

Uranyl species are less prone to hydrolysis than U(IV) and consequently colloids play a less significant role in the near surface transport of uranium than thorium [174]. An important exception to this general rule occurs in organic-rich environments, such as peat bogs. High molecular weight organics (humic acids) possess a strong affinity for uranium and spectroscopic studies indicate that it is bound in the U(VI) state [175].

### **3.2.2. Solid geochemistry**

Uranium is not a particularly rare element. It has been estimated that more than 5% of all known minerals contain uranium as an essential constituent [176]. Present in a wide range of geochemical environments uranium is now considered to be a more abundant constituent of the earth's crust than either cadmium or mercury. The number of discrete mineral phases identified is almost 200. These comprise 'primary' (U(IV)) oxides, silicates, phosphates and carbonates and a wide array of 'secondary' (U(VI)) phases containing common and less abundant groundwater anions [177].

Uranium is a relatively mobile element in the near surface zone owing to the stability of U(VI) aqueous complexes. However, it may be precipitated by reduction to U(IV) or in the form of uranyl minerals, principally phosphates, silicates, arsenates, vanadates and oxyhydroxides, several of which may occur simultaneously at the same locality [177]. Around 150 such phases have been identified and their formation represents the dominant fixation mechanism for uranium in weathering environments [177]. It follows that the amount of uranium released to ground- or surface waters from these secondary sources will depend on the solubility and dissolution rate of the phases as a function of pH and water composition.

Experimental studies of uranium solubility have focused on the behaviour of  $\text{UO}_2$  owing to the resources devoted to spent fuel processing and disposal [178]. While these data are useful in a broader context, it has to be borne in mind that natural uranium oxides differ in several important respects from spent fuel. The most common ore mineral, pitchblende, contains mixed oxides ( $\sim\text{U}_3\text{O}_8$ ) and even natural uraninite ( $\text{UO}_2$ ) is structurally and chemically distinct. In addition to mineral impurities, uraninite contains radioactive decay products from thorium to lead and these represent several weight per cent. Spent fuel, in contrast, does not contain substantial progeny but does

incorporate trace fission and activation products together with small quantities of the transuranic elements.

Increasing concerns surrounding the potential health effects of depleted uranium have prompted research into the corrosion of uranium metal in diverse chemical environments [179]. These studies reveal widely disparate dissolution rates, depending on the composition of the aqueous solution, and complex reaction sequences. The evolving assemblage of metastable phases that develop on the surface cannot be predicted solely from considerations of thermodynamic equilibrium.

Once oxidized, an enormous variety of uranyl phases can precipitate from groundwater solutions, including phosphates, silicates, oxyhydroxides, sulphates, arsenates, vanadates and carbonates. Indeed, it is common in nature to find several U(VI) minerals coexisting on weathered ores. Developing an understanding of the paragenesis and phase relationships among these is essential for predicting the environmental fate of uranium-bearing residues. Burns and Finch [177] give a detailed and systematic classification of uranium mineralogy, serving to emphasize the scale of the task.

The first OECD/NEA TDB review of uranium, which appeared in 1992 [161], lists free energy values and formation reaction constants for a variety of uranium oxides and more than 150 other solids. The latter largely comprise halide compounds. Surprisingly, the review lacked any meaningful discussion of uranium mineralogy and did not contain recommended thermodynamic data for even the more common uranium minerals. Its usefulness for practical applications in geochemistry was questionable and the oversight prompted a reappraisal by the OECD/NEA. This led, in turn, to the addition of a short section on uranium minerals in the subsequent review of americium chemistry [180].

According to the OECD/NEA review team, relatively few publications were overlooked during the original study and the data contained in these documents did not merit inclusion in the final selection. The reasons given were the absence of information on experimental methods or auxiliary data, errors in activity correction and failure to control or report on the background electrolyte [180]. No doubt these criticisms were justified and provide a fair reflection of the quality of data available for modelling studies.

However, as noted previously, the selection criteria applied within the OECD/NEA TDB are more stringent than those typically employed by workers engaged in practical applications. It is preferable to perform calculations with uncertain data and to compare the results with field or laboratory observations than to ignore the possibility that such phases may form. Whereas the former might give misleading results, geochemical modelling studies using only strictly authenticated data would certainly give erroneous results because

possibly relevant and important species would not be considered. Consequently, databases used for nuclear waste disposal studies or uranium mining applications supplement the OECD/NEA data set with values from other sources (see Section 4.2).

### 3.2.3. Adsorption/desorption behaviour

A fairly extensive literature exists on the adsorption of uranium on natural matrices. In addition to simple partitioning measurements, these include mechanistic studies of uranium uptake by oxides and hydroxides [181, 182], clay minerals and silica [183, 184] and organics [185, 186].

Hsi and Langmuir [181] give surface properties of amorphous iron oxyhydroxide, goethite and haematite, providing sorption constants for uranium hydroxide and carbonate species onto goethite. The authors note that the adsorption process is not entirely reversible, desorption kinetics tending to be slower. Similar findings were obtained from dynamic flow through tests using the well-characterized Clashach sandstone [187].

Uranium(VI) uptake on goethite and colloidal magnetite was also explained in terms of surface complexation modelling by Missana et al. [188, 189]. In neither case was desorption explored in detail, even though anoxic conditions, under which the uranium may have been reduced, were employed in some tests.

Other investigations of the same system [190, 191] have sought to interpret the data as representing stages in the progressive incorporation of uranium into the iron oxide lattice. According to Duff et al. [191], following surface adsorption of the uranyl ion, structural rearrangement occurs allowing the much smaller  $U^{6+}$  ion to be accommodated as uranate. Only limited substitution is possible, such that beyond the saturation point excess uranium is released leading to the precipitation of discrete uranyl phases, e.g. schoepite  $UO_2(OH)_2$ . This interpretation accords well with observation of natural systems and is supported by EXAFS results.

The uranium-iron hydroxide system was also investigated by Waite et al. [182]. The constants derived from their work are often quoted, particularly in the waste disposal literature. There is no doubt that they give a satisfactory description of the laboratory titrations carried out. However, the original aim of the study was to account for retardation of uranium in a near surface dispersion plume at the Koongarra deposit, northern Australia. Detailed re-evaluation of uranium 'sorption' at this site revealed the presence of previously unidentified, microcrystalline uranium-bearing phases, demonstrating again the overriding importance of secondary mineralization [192].

Uranium can be removed very effectively from solution by organic matter. Although the processes are not fully understood, it is generally believed that U(VI) species are initially complexed by carboxylic groups on the organic molecule [185]. The reversibility of the process was studied by Read et al. [175] who demonstrated that release to solution could only be effected by lowering the pH. Once attached, the uranium may be reduced to U(IV), accounting for the very high concentrations (several per cent) reported in peat. A recent attempt to model U(VI) sorption to haematite in the presence of humic acid is described by Lenhart and Honeyman [193].

#### **3.2.4. Microbiological interactions**

The dissimilative reduction of uranium was first described for the Fe(III) reducing bacteria *Geobacter metallireducens* [194, 195], where the electron donor is acetate. *Shewanella putrefaciens* can grow using U(VI) only as electron acceptor and hydrogen as electron donor. A protein located on the cell surface of *Geobacter sulfurreducens* plays a role in the extracellular reductive precipitation of U(IV). Some species of *Desulfovibrio* can also reduce U(VI) by enzymatic processes, using hydrogen or lactate as electron donor [196], but are unable to grow using uranium as the only electron acceptor. Other sulphate reducing bacteria are able to carry out a dissimilative reduction of uranium, e.g. *Desulfotomaculum reducens* MI-1 [197] and *Desulfovibrio* UFZ B 490 [198]. *Desulfovibrio vulgaris* is the only organism in which the enzyme system responsible for U(VI) reduction has been characterized in detail [133, 199]. The bacterial reduction of soluble U(VI) to insoluble U(IV) is an important process in the global cycle of uranium. In anaerobic sediments, this reaction is the main process for uranium fixation [200, 201]. The potential of bacteria for bioaccumulation of uranium has been investigated by Selenska-Probell et al. [202, 203]. Their results for a number of ubiquitous soil microbes (e.g. strains of *Pseudomonas*) indicate accumulation of uranium in the form of sparingly soluble phosphate compounds.

### **3.3. GEOCHEMISTRY OF NEPTUNIUM**

#### **3.3.1. Aqueous chemistry**

Neptunium was the first of the transuranic elements discovered in 1940 following the irradiation of uranium foils with slow neutrons. Almost 20 isotopes have now been identified with half-lives ranging from a few seconds to more than 2 million years ( $^{237}\text{Np}$ ). Neptunium is now known to occur naturally,

albeit at very low concentrations, as a result of neutron induced transmutation of uranium ores.

The chemistry of neptunium is complex and unique, though its behaviour does resemble the trivalent and tetravalent lanthanides in some respects and uranium in others. It occurs in oxidation states (III) to (VII) of which the tetravalent and pentavalent states are the most relevant to the natural systems considered here [159, 204]. The Np(III) state is more stable to oxidation than U(III) and the  $\text{Np}^{3+}/\text{Np}^{4+}$  couple is reversible. The  $\text{Np}^{4+}/\text{NpO}_2^+$  couple is also reversible, but the kinetics tend to be slow; rates depending on the media [159]. Once formed, the pentavalent state ( $\text{NpO}_2^+$ ) is much more stable than the corresponding  $\text{UO}_2^+$  and less prone to hydrolysis than Np(IV).

In aqueous solution, Np(IV) forms stable complexes with a number of common anions, including sulphate, fluoride and nitrate, as well as with simple organic ligands. Phosphate complexes have also been proposed [205] but were rejected by the OECD/NEA TDB review group [204]. The reasons given were similar to those cited for the corresponding uranium system [161]. The hydrolysis of  $\text{Np}^{4+}$  is comparable to that of  $\text{U}^{4+}$  proceeding to the formation of polymeric species. This behaviour contrasts sharply with  $\text{NpO}_2^+$ , a large ion with a single charge. Although one might expect only weak complexation, Np(V) does form stable complexes, particularly with carbonate. The research of Kim and co-workers [206, 207], who studied the resulting species using modern spectroscopic techniques, is noteworthy and has led to a reasonably coherent data set for modelling.

Choppin [208, 209], Eriksen et al. [210] and Langmuir [211], among others, discuss the environmental speciation of neptunium, while Philips [212] and Allard [213] attempted early compilations of relevant constants. However, the most thorough review of the available data is undoubtedly that of Lemire et al. [204]. Their recommended data set comprising fifty formation constants compares favourably with that of uranium, an element that has been studied for a far longer period. The information contained in this book provides the basis for other listings [164]. Current research trends suggest that the recent update [168] will itself need to be revised soon, as sensitive techniques for in situ speciation studies become more widely available.

One of the principal areas of outstanding concern surrounds the potential complexation of neptunium (and the other transuranic elements) by organic acids, either natural ‘humics’ and ‘fulvics’ or degradation products of cellulose and co-disposed waste. The indication from preliminary studies is that such materials could significantly enhance solubility but quantifying their importance requires further research.

### 3.3.2. Solid geochemistry

The occurrence of natural neptunium ( $^{239}\text{Np}$  from neutron capture by  $^{238}\text{U}$ ) in uranium ore bodies is a tenuous guide to its likely geochemical behaviour because of the very small amounts present. In the normal course of reactor operation,  $^{237}\text{Np}$  with a half-life of  $2.1 \times 10^6$  a is produced in significant quantities, most of which is concentrated with the fission products following plutonium recovery. Such waste would be consigned to a geological repository. Residual neptunium in spent fuel is also destined for deep disposal in those countries that do not reprocess fuel. However, the fact that depleted uranium contains measurable amounts of neptunium implies a component of reprocessed material and one pathway along which it can enter the near surface environment [179].

Calculation of source terms for released nuclides is not straightforward even with spent uranium fuel. Whereas the major controls on dissolution of the  $\text{UO}_2$  matrix itself are reasonably well established, this is certainly not the case for trace transuranic and fission product impurities. Johnson and Tait [214] provide an outline of the issues with respect to performance assessment studies in Sweden. Subsequent to leaching, the solid phases likely to incorporate neptunium in different geochemical settings are also uncertain. It is improbable that it would be concentrated sufficiently to form a discrete neptunium phase. However, as noted above, uranium and thorium mineralogies are complex and there is ample evidence of such behaviour from other highly charged ions, including zirconium and the rare earths.

A more realistic outcome would be the substitution of neptunium for other cations in secondary alteration phases, in which case the prevalent oxidation state is all important. The oxidation states, principally  $\text{Np(IV)}$  and  $\text{Np(V)}$ , will display markedly different associations in terms of co-precipitation. The highly charged  $\text{Np}^{4+}$  ion readily substitutes for thorium in a range of synthetic phosphates and silicates [215]. Indeed, artificial matrices based on the lanthanide phosphate monazite have been proposed as potential waste forms for transuranic-rich streams. Conversely,  $\text{NpO}_2^+$  could replace the uranyl ion in the various  $\text{U(VI)}$  phases discussed above.

Co-precipitation of transuranics with uranium, thorium or the rare earths has been postulated as an important retention mechanism and one that is currently overlooked in waste disposal programmes [177, 216]. The reasons given for this omission are the paucity of suitable thermodynamic data to parametrize solubility models and the fact that these elements are present at low concentrations. The first is not in itself justification for the use of empirical ‘equilibrium distribution coefficients’ since they do not represent the same process. Further, many elements present in solution at extremely low mass

concentrations are subject to solubility control in the environment. They include radium, which is readily fixed in baryte, and polonium, both radiological significant components of NORM [217–219].

Solubility products for eleven neptunium solids are given by Lemire et al. [204]: four oxides/hydroxides, six carbonates and a fluoride ( $\text{Na}_3\text{NpF}_8$ ). Gibbs free energy and/or enthalpy data are listed for around twenty other solids, mainly halides. These phases are almost certainly not those that would govern neptunium solubility in groundwater systems. Other sources of neptunium data, including those accompanying advanced modelling software [220], are similarly deficient.

### **3.3.3. Adsorption/desorption behaviour**

There are few published studies into the adsorption of neptunium [221]. Bidoglio et al. [222] conducted static and flow through tests of migration through clay–sand columns, deriving a model for the chromatographic separation of individual neptunium species. The observations were attributed to slow reaction kinetics. Stammose et al. [223] found that uptake onto clay-rich sand was irreversible over the timescales of their experiments. Related work in Canada [224] found that retardation of  $^{237}\text{Np}$  through columns of crushed granite was similarly dependent on flow rate. Turner et al. tried to explain their experimental results in terms of a surface complexation model [97].

Laboratory experiments into neptunium uptake from seawater by marine sediments indicate that  $\text{Np(IV)}$  and  $\text{Np(V)}$  species exhibit different kinetics [225]. For  $\text{Np(IV)}$ , rapid initial uptake was followed by desorption over longer periods. In contrast, initial sorption of  $\text{Np(V)}$  was followed by further uptake, albeit at a slower rate, rather than desorption.

All of these studies suggest that equilibrium partitioning, whether using simple distribution coefficients or more sophisticated surface complexation models, is not an appropriate means of accounting for retention of neptunium on geological matrices. Nevertheless, some authors have persisted with the approach, even attempting to derive  $K_d$  values as a function of redox potential [226] or humic acid concentration [227].

### **3.3.4. Microbiological interactions**

Most studies of the interaction between neptunium and microorganisms have been dedicated to the biosorption and bioaccumulation of neptunium. Some investigations have shown the capacity of some microorganisms such as *Shewanella putrefaciens* [136] or a sulphate reducing consortium [228] to



reduce Np(V) to Np(IV) in anaerobic conditions. The biochemical mechanisms involved in this reduction are not identified.

### 3.4. GEOCHEMISTRY OF TECHNETIUM

#### 3.4.1. Aqueous chemistry

Technetium was the first element to be produced artificially and 21 isotopes have now been identified. The longest lived is  $^{98}\text{Tc}$  with a half-life of  $4.2 \times 10^6$  a, but the most important from an environmental perspective is  $^{99}\text{Tc}$  (half-life  $2.13 \times 10^5$  a), a high yield product (6.1 %) from thermal neutron fission of  $^{235}\text{U}$  and fission of  $^{239}\text{Pu}$  (5.9%). Most of the technetium generated in civil reactors finds its way to high level waste streams following reprocessing and several tonnes are produced annually. Over the years, large quantities have been discharged to the marine environment. The rationale behind this 'dilute and disperse' policy was the perceived high mobility of technetium under oxidizing conditions [229]. However, knowledge of its long term fate in the environment is limited and concerns have been raised now that the element has been shown to accumulate in marine biota, notably lobsters and certain types of seaweed [230].

For an introduction to early work on the environmental behaviour of technetium the reader is referred to Desmet and Myttenaere [231] and Bishop et al. [232]. Additional papers of relevance can be found in Bulman and Cooper [233], which also introduces speciation modelling under near surface conditions and uptake by plants and soils. Lemire and Garisto [234] and Puigdomenech and Bruno [235] carried out reviews of technetium chemistry from the perspective of nuclear waste disposal applications.

Until recently, numerical models drew heavily on the compilation of thermodynamic data published by Rard [236]. Even though this was acknowledged to be incomplete and subject to considerable uncertainty, it served to highlight the overriding importance of redox state in determining environmental mobility. This author was a key contributor to the more extensive review carried out under the auspices of the OECD/NEA [237] that provides the basis for most current modelling studies. The outcome of the review is summarized below.

Technetium chemistry is complex, characterized by valencies ranging from -I to +VII and a tendency to form binuclear and polynuclear species. Of the various oxidation states exhibited by technetium, the heptavalent and tetravalent are the most important in aqueous solution. The pertechnetate ion,  $\text{TcO}_4^-$ , is the stable form in contact with air over the entire pH range [237] and

would be expected to predominate under near surface conditions. Even under nominally oxygen free conditions, partial oxidation of dissolved Tc(IV) species is thought to occur.

The  $\text{TcO}_4^-$  ion can be reduced by halides in strongly acidic solutions, the rates of reaction following the trend  $\text{I}^- > \text{Br}^- > \text{Cl}^-$  and the rate increasing with acidity and temperature. The relative stability of Tc(IV) halides follows the same trend. However, species such as  $\text{TcCl}_6^{2-}$  would undergo complete hydrolysis in groundwaters. Gamma radiolysis can also induce reduction where concentrations are high ( $>5 \times 10^{-4}$  M) [237]. Organic matter and biologically mediated reactions may lead to fixation of technetium as Tc(IV) but the precise mechanisms are poorly understood and difficult to quantify. Bioaccumulation of technetium has been reviewed by Bishop et al. [232].

Despite the considerable efforts made in the past thirty years, the current level of knowledge of the aqueous chemistry of technetium is insufficient for predictive modelling in natural media. Thermodynamic data for the pertechnetate–water system and hydrolysed forms of Tc(IV) are felt to be reasonably complete and of acceptable quality but there is a lack of information for complexes with even simple inorganic ions [168, 237]. The situation for organic complexes is even worse. The OECD/NEA TDB contains selected formation reactions and associated constants for only nine aqueous species. Owing to the absence of enthalpy or heat capacity data the values are not applicable to temperatures above 25°C.

### 3.4.2. Solid geochemistry

Several authors have detected technetium in alteration products arising during the leaching of spent fuel. The high solubility of technetium under oxidizing conditions and the stability of the pertechnetate ion suggest that mineralization reactions would not play such an important role in technetium immobilization as with the elements addressed above. For completeness, the state of the thermodynamic database with regard to technetium solids is described briefly before discussing surface reactions in the next section.

According to Rard et al. [237], reasonable data exist for  $\text{TcO}_2$ ,  $\text{Tc}_2\text{O}_7$  and the less soluble pertechnetate salts (e.g.  $\text{KTcO}_4$ ). Even here, there are inconsistencies in the reported solubility of  $\text{TcO}_2$  as a function of pH, data varying by about three orders of magnitude across most of the range. Very few heat capacity measurements have been reported that would allow extrapolation of the available constants to higher temperatures. The  $\text{Tc}_2\text{O}_7$  salt is hygroscopic, deliquescing in air and so of little relevance to the systems considered in this report.

New data are needed urgently for  $\text{TcS}_2$  and  $\text{Tc}_2\text{S}_7$ , since there is potential for retention by sulphide minerals. The available solubility data are regarded with suspicion owing to the presence of colloidal material.

Technetium has a tendency to form intermetallic compounds, several of which are described by Rard et al. [237], although hard data are lacking. There are no data at all for interactions with silicate. The authors of the OECD/NEA review [237] highlight gaps in the database as an indicator for further experimental work. In view of the fact that constants are recommended for only 9 aqueous species and 15 solids, some of which are not environmentally relevant, defining priorities is barely an issue.

#### **3.4.3. Adsorption/desorption behaviour**

Numerous examples of technetium sorption onto rocks or mineral phases are to be found in the literature, the vast majority empirical in nature. Vandergraaf et al. [238] studied the sorption of technetium onto a variety of minerals under both oxic and anoxic conditions. Their findings indicate that very little uptake occurs in the presence of oxygen but that under reducing conditions it is taken up by iron-containing phases. Whether this required prior reduction of the technetium itself was not clear.

Other investigations of the influence of redox potential on technetium sorption [239–241] support these observations and, additionally, note the importance of ionic strength. According to Lieser and Bauscher [239], sorption of pertechnetate onto sediments is inhibited at high salinity, possibly due to competition from chloride. Conversely, sorption of  $\text{Tc(IV)}$  is accelerated by high salt concentrations. Again, however, it was not clear whether reduction led to the formation of sparingly soluble phases such as  $\text{TcO}_2$ . If this were the case then the process would be better described in terms of precipitation. Indeed, as noted by Amaya et al. [241], ‘sorption’ of technetium under reducing conditions is irreversible.

#### **3.4.4. Microbiological interactions**

*Shewanella putrefaciens* and *Geobacter metallireducens* are able to reduce  $\text{Tc(VII)}$  with an enzymatic mechanism [242]. Other studies underlined similar activities with *Rhodobacter sphaeroides*, *Paracoccus denitrificans*, some pseudomonades and a range of sulphate reducing bacteria [199]. In anaerobic conditions, *Escherichia coli* can couple the formate or hydrogen oxidation step with the  $\text{Tc(VII)}$  reduction, precipitating the radionuclide within the cell [243]. It seems that a complex formate hydrogenlyase located in the periplasm of the strains is involved in the reduction of  $\text{Tc(VII)}$  [244]. Recent studies have shown

that Tc(VII) can be reduced via indirect microbial processes (e.g. via biogenic sulphide, Fe(II) or U(IV) [199]). Owing to these bacterial properties, some studies focused on bioprocess development for remediating Tc(VII) contaminated water using immobilized cells of sulphate reducing bacteria [244].

### 3.5. GEOCHEMISTRY OF CAESIUM

#### 3.5.1. Aqueous chemistry

Caesium behaves like potassium in both the environment and the human body [112]. Its fission products include three main isotopes at significant concentrations:  $^{134}\text{Cs}$  ( $T_{1/2} = 2.05 \text{ a}$ ),  $^{135}\text{Cs}$  ( $T_{1/2} = 3 \times 10^6 \text{ a}$ ) and  $^{137}\text{Cs}$  ( $T_{1/2} = 30.23 \text{ a}$ ).

Being an alkali metal, caesium occurs in solution primarily as the single charge cation and forms only weak complexes. Stability/formation constants of caesium species are generally low. Hence, the dominant aqueous species in most ground- and surface waters is the uncomplexed  $\text{Cs}^+$  ion [112].

#### 3.5.2. Solid geochemistry

The solubility of most caesium compounds is very high: precipitation reactions are not expected to control caesium's geochemical behaviour.

#### 3.5.3. Adsorption/desorption behaviour

In general, most soils sorb caesium rather strongly and often selectively. Some micaceous minerals, such as illite and vermiculite, tend to take up caesium in their intrastructural layers [245–247]. Thus, the high retention of caesium in soil and sediments is determined by two different processes: structural fixation and reversible selective sorption [248]. Reversible selective sorption occurs on frayed edge sites, located at the edges of micaceous clay particles [246]. The ability of a solid to sorb caesium selectively is characterized by the capacity of the frayed edge sites or by a so-called radiocaesium interception potential, which is the product of the frayed edge site capacity and the selectivity coefficient for  $^{137}\text{Cs}$  compared with a competing ion [249]. Cremers and co-workers [246, 249] developed a special method for the quantitative determination of the frayed edge site capacity and the radiocaesium interception potential.

The interlayer distance between the sheets of certain micaceous minerals excludes diffusion of some major ions, such as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , owing to their comparatively large ionic radii, while permitting the  $\text{Cs}^+$  ion to fit perfectly between the layers. Although fixation of  $\text{Cs}^+$  ions as well as  $\text{K}^+$  and

$\text{NH}_4^+$  ions had earlier been attributed to their close fit within the hexagonal cavities of basal oxygen planes, the low hydration energy of the ions is now considered to be the major factor in their fixation [245]. The  $\text{Cs}^+$ ,  $\text{NH}_4^+$  and  $\text{K}^+$  cations, having low hydration energy, effect interlayer dehydration and layer collapse and become, therefore, fixed in interlayer positions [245]. Conversely, cations with high hydration energy, such as  $\text{Sr}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{Li}^+$ , result in expanded interlayers and are not fixed. Hence, these micaceous minerals exhibit a very high selectivity and fixation capability for  $\text{Cs}^+$  compared with the main cations in natural systems. Even a small amount of these mica–clay minerals in a soil may selectively fix a large amount of caesium, resulting in lower mobility in the environment and lower bioavailability [250, 251].

#### **3.5.4. Microbiological interactions**

Studies on the interaction between bacteria and caesium have indicated bioaccumulation by bacteria such as *Escherichia coli* [252] and *Pseudomonas fluorescens* [253], by cyanobacteria and algae such as *Anabaena variabilis* and *Chlorella salina* [254, 255] and by fungi [256].

### **3.6. GEOCHEMISTRY OF STRONTIUM**

#### **3.6.1. Aqueous chemistry**

The only strontium isotope of concern in the environment is  $^{90}\text{Sr}$  ( $T_{1/2} = 29.1$  a), a fission product. As a consequence of atmospheric testing of nuclear weapons,  $^{90}\text{Sr}$  is distributed globally. In the environment and in the human body, strontium behaves like calcium (hence strontium is a ‘bone seeker’).

There is little tendency for strontium to form complexes with inorganic ligands [112]. The solubility of the free  $\text{Sr}^{2+}$  ion is not significantly affected by the presence of most inorganic anions. Dissolved strontium forms only weak aqueous complexes with carbonate, sulphate, chloride and nitrate. Strontium is also not expected to form strong complexes with natural organic substances, such as humic and fulvic acids.

Observations and calculations show that strontium exists in ground- and surface waters as the uncomplexed ion  $\text{Sr}^{2+}$ . This ion dominates strontium speciation throughout the pH range of 3–10. Between pH 3 and 8.5, the  $\text{Sr}^{2+}$  species constitutes approximately 98% of the total dissolved strontium. As the pH increases above 9, the  $\text{SrCO}_{3(\text{aq})}$  is calculated [112] to be between 2% and 12% of the total dissolved strontium. As the pH increases above 9, the  $\text{SrCO}_{3(\text{aq})}$  becomes increasingly important.

### 3.6.2. Solid geochemistry

Since strontium generally occurs in nature at much lower concentrations than calcium, it does not commonly form pure phases but co-precipitates with calcite and anhydrite. Strontium can also co-precipitate with barium to form  $(\text{Ba}_{(1-x)}\text{Sr}_x)\text{SO}_4$  in more alkaline environments [112].

### 3.6.3. Adsorption/desorption behaviour

As is the case for caesium, cation exchange is the most important mechanism for strontium retention in the geosphere. Hence, the cation exchange capacity is a controlling parameter [112, 257]. Some authors have reported that strontium adsorption is completely reversible [258]. Recent data seem to indicate that fixation of strontium takes place in two stages, with time constants of several weeks and around 100 years, respectively [259].

### 3.6.4. Microbiological interactions

Studies have demonstrated the biomineralization of strontium by metabolizing bacteria [260] and cyanobacteria [261]; strontium being precipitated as crystalline strontium carbonate. Other studies have shown strontium accumulation by bacterial or fungal cells [262].

## 3.7. GEOCHEMISTRY OF THORIUM

### 3.7.1. Aqueous chemistry

Thorium occurs in only one oxidation state (+IV) in nature. The available thermodynamic data for thorium aqueous species and solids have been compiled and critically reviewed by Langmuir and Herman [263] in an analysis of the mobility of thorium in low temperature natural waters. Thorium undergoes hydrolysis in aqueous solutions at pH values above 3. Numerous mononuclear and polynuclear hydrolysis species are reported, including  $\text{Th}(\text{OH})_2^{2+}$ ,  $\text{Th}_2(\text{OH})_2^{6+}$ ,  $\text{Th}_4(\text{OH})_8^{8+}$ ,  $\text{Th}_4(\text{OH})_{12}^{4+}$  and  $\text{Th}_6(\text{OH})_{15}^{9+}$ , but the mononuclear species in particular are usually relatively minor species in the solution. At pH values higher than 3.5, the hydrolysis of thorium is dominated, in order of increasing pH, by the aqueous species  $\text{Th}(\text{OH})_2^{2+}$ ,  $\text{Th}(\text{OH})_3^+$  and  $\text{Th}(\text{OH})_{4(\text{aq})}$ . In addition to undergoing hydrolysis, thorium can also form various aqueous complexes with inorganic anions such as fluoride, phosphate, chloride and nitrate. Below pH 5, thorium speciation is dominated by thorium

fluoride complexes. Between pH 5 and 7, dissolved thorium is predicted to be dominated by thorium phosphate complexes and this phosphate complexation is expected to have a role in the mobility of thorium over this range of pH values [263]. In this higher pH region, the dissolved thorium concentrations are very low and only the unhydrolysed  $\text{Th}^{4+}$  ion and/or mononuclear divalent hydrolysis species ( $\text{ThOH}^{3+}$ ,  $\text{Th}(\text{OH})_2^{2+}$ ) are expected to be important in the absence of other ligands [264]. However, thorium concentrations may become elevated owing to formation of thorium–carbonate complexes.

### **3.7.2. Solid geochemistry**

The main thorium containing minerals (thorite, thorianite, zircon and monazite) are resistant to weathering and do not dissolve readily in ground- or surface waters. Hydrous thorium oxide, the dominant forms of Th(IV) in aqueous environments, is known to precipitate in the natural environment and is likely to alter with time to a more crystalline solid that has a lower solubility. The solubility of hydrous Th(IV) oxides decreases with increasing pH. At higher pH values, the hydrous oxides precipitate and dissolved thorium concentrations decrease rapidly. It is rather immobile in the aqueous environment owing to the low solubility of thorianite but the high particle reactivity of thorium shows strong colloidal characteristics, hydroxide and silicate colloids allowing transport of thorium in insoluble form. The movement of thorium is therefore controlled mainly by physical processes [112].

### **3.7.3. Adsorption/desorption behaviour**

In groundwater, thorium may adsorb or precipitate onto colloids (colloids may consist of precipitates, bacteria, organic matter, and suspended rock and minerals fragments) reversibly or irreversibly. Evidence indicates that around 10–17% of the total thorium contents of groundwater at the Koongarra, Australia, uranium deposits were present in a colloidal form [40]. Therefore, thorium is largely transported in particulate form. Thorium generated in solution by radioactive decay of uranium, rapidly hydrolyses and sorbs onto solid surfaces, including colloids. Other substrates controlling thorium concentrations to very low levels in ground- and surface waters are humic substances. Thorium organic complexes are likely to have an important effect on the mobility of thorium in soil–water systems. Thorium is believed to form stronger complexes with dissolved organics than uranium [263]. Ligands such as oxalate, citrate and ethylenediaminetetraacetic acid (EDTA) are able to enhance thorianite solubility significantly. This effect, however, decreases sharply above a pH of 7, when thorium tends to sorb almost completely onto clays and solid

organic matter. A better understanding of the role of organics in enhancing thorium mobility is limited by the paucity of thermodynamic data, exacerbated by the relatively slow reaction rates in most natural environments [40]. Iron and manganese oxides are expected to be more important adsorbents of thorium than silica.

#### **3.7.4. Microbiological interactions**

There appear to be no studies showing a direct biotransformation of thorium by soil microorganisms; only the mechanisms of biosorption, bioaccumulation and bioprecipitation are described in the literature [122].

### **3.8. GEOCHEMISTRY OF RADIUM**

#### **3.8.1. Aqueous chemistry**

Radium has a distinctive chemistry compared with the actinides since it is an alkali earth element. Chemically radium behaves in a manner similar to barium and since alkali earth elements are highly electropositive, radium does not undergo hydrolysis over a wide pH range and is present in solution as a simple ion, i.e. as  $\text{Ra}^{2+}$ . On the basis of thermodynamic data from Langmuir and co-workers [265, 266] and Sturchio et al. [267], it is possible to calculate that the dominant aqueous radium species would almost always be  $\text{Ra}^{2+}$ , while the next most abundant species are  $\text{RaCl}^+$  and  $\text{RaSO}_4^0$ .

The removal of radium from solution can occur by hydrolysis, adsorption and formation of insoluble salts; these factors affect radium concentrations in ground- and surface waters.

#### **3.8.2. Solid geochemistry**

The large ionic radius of radium makes it incompatible for uptake in most minerals, but minerals that accommodate barium generally also take up large amounts of radium [40]. Co-precipitation with barium compounds is common and some co-precipitation occurs with calcium, magnesium and iron to form sulphate and carbonate minerals such as calcite ( $\text{CaCO}_3$ ), gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and baryte ( $\text{BaSO}_4$ ) [268, 269]. If the latter mineral is formed in a uranium-rich environment, it may become highly radioactive because of the barium/radium substitution. In general, radium is only slightly soluble compared with calcium and strontium and its solubility is controlled by the concentration of sulphate or carbonate ions [40]. In very acidic water, typical



of acid mine drainage for instance, co-precipitation with amorphous silica also seems to be an important but little recognized radium fixation process [269].

### **3.8.3. Adsorption/desorption behaviour**

Radium is efficiently fixed on soils, but a large part of its uptake is reversible [122]. This reversible uptake is likely to be linked to sorption phenomena. It has been shown experimentally that radium sorbs easily onto natural soils and sediments [270] and onto almost all of their primary constituents, including ferric hydroxides, quartz, muscovite, albite, clay minerals, carbonates, aluminium oxides and organic matter [122, 271–274].

The degree of sorption depends on several variables owing to the multiple modes of interaction between radium and the soil and sediment mineral matrix. The most important ones are the ionic strength of the solution and the particle surface area. For instance, a decrease in radium sorption can be observed with increasing salinity and this has been attributed to a variety of effects including competition of cations for available sorption sites [267]. Divalent cations, such as  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$  and  $\text{Mg}^{2+}$ , occupy sorption sites that are also suitable for radium. These observations are in line with the alkali earth nature of radium. These elements are likely to undergo cation exchange on clay minerals. A selectivity coefficient for radium on this type of surface has been estimated on the basis of the one for  $\text{Ca}^{2+}$  [275]. Furthermore, an increase in the mineral surface charge, the increased stability of inorganic radium complexes in high ionic strength solutions and the formation of strong organic complexes serve to decrease radium sorption [267].

### **3.8.4. Microbiological interactions**

The biosorption of radium has been studied in detail with different biomass types, mainly fungi. For example, *Penicillium chrysogenum* is able to accumulate large amounts of radium present in solution [276]. In contrast, indirect solubilization of radium from stored uranium-bearing tailings can result from conversion of sulphate to sulphide and results in the dissolution of some baryte which, in turn, releases small amounts of radium [277, 278]. In addition, radium release is enhanced by bacterial reduction of manganese and iron oxides in the uranium mill tailings environment [279].

### 3.9. GEOCHEMISTRY OF LEAD

#### 3.9.1. Aqueous chemistry

Lead has three known oxidation states, 0, +2 and +4; the most common redox state encountered in the environment being the divalent form. The solubility of lead in aqueous solutions is rather low. This solubility can be enhanced by the presence of complexing agents, such as chloride, nitrate, carbonate and organic ligands. The speciation of lead in natural waters is quite complex and may be strongly influenced by the availability of organic complexing agents, for which lead has a high affinity. In most natural waters at pH values above 7, aqueous lead exists mainly as carbonate complexes,  $\text{PbCO}_{3(\text{aq})}$  and  $\text{Pb}(\text{CO}_3)_2^{2-}$ . Within the pH range of 6.7–7.5, the main species of lead appear to be the free ionic species  $\text{Pb}^{2+}$  and the neutral complex species  $\text{PbCO}_3^0$ . Between pH 7 and 9 the latter species dominates the species distribution. At pH values above 9, in addition to  $\text{PbCO}_3^0$ , a significant fraction of soluble lead is present as the anionic carbonate complex  $\text{Pb}(\text{CO}_3)_2^{2-}$  [162].

#### 3.9.2. Solid geochemistry

Lead solids may occur in the environment in a number of mineral forms, including carbonate ( $\text{PbCO}_3$ , cerussite), sulphide ( $\text{PbS}$ , galena), sulphate ( $\text{PbSO}_4$ , anglesite), chromate ( $\text{PbCrO}_4$ , crocoite), phosphate ( $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ , pyromorphite) and oxides ( $\text{PbO}$ ,  $\text{Pb}_3\text{O}_4$ ) [280]. In addition, scales formed in natural gas wells have been shown to contain lead in almost pure metallic form and also in the form of a lead–mercury alloy [94]. These extremely hazardous scales contain activity concentrations of  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  in excess of 4000 Bq/g. Limited secondary lead minerals may control the concentration of dissolved lead in soil/water environments (e.g. plumbogummite,  $\text{PbAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$ ) [281]). If the concentration of lead in a pore water or groundwater exceeds the solubility of any of these phases, the lead containing solid phase will precipitate and thus control the maximum concentration of any lead remaining in the aqueous phase. Lead may also exist in soils as solid solution phases. Solid solutions are defined as solid phases in which a minor element will substitute for a major element in the mineral structure. Lead may occur as a minor replacement in baryte, apatite, calcite and iron sulphides [282, 283]. Consequently, the equilibrium solubility of lead controlled by these phases will be less than the concentrations controlled by corresponding pure phases, namely  $\text{PbSO}_4$ ,  $\text{Pb}_5(\text{PO}_4)_3\text{OH}$ ,  $\text{PbCO}_3$  and  $\text{PbS}$ . Under reducing conditions, galena may control lead concentration in the environment and may incorporate  $^{210}\text{Pb}$  by

isotopic substitution. Within the pH range of 6–9, the equilibrium solubility of galena would control lead concentrations at levels of less than 21 ng.

### **3.9.3. Adsorption/desorption behaviour**

Lead is known to sorb onto soils' constituent surfaces such as clays, oxides, hydroxides and organic matter. Among these constituents, organic matter and especially humic acids play a major role in effecting the low mobility of lead in organic rich soils [284]. Studies on lead adsorption on oxide and hydroxide minerals show that substrate properties such as the specific surface and degree of crystallinity control the degree of the adsorption [280], e.g. manganese oxides sorbing lead more efficiently than iron oxides [285]. Studies on clay minerals have shown that at acidic pH values and low ionic strength lead is adsorbed by exchange onto clays, readily replacing calcium and potassium, while beyond neutral pH, precipitation reactions and/or specific surface interaction such as surface complexation may control lead concentrations in solution rather than ion exchange [286, 287]. High specificity of adsorption on oxide and hydroxide surfaces and the relatively poor desorption of adsorbed lead indicated that upon adsorption lead forms solid solutions with oxide and hydroxide surfaces. In addition, the presence of very strong chelating ligands dissolved in solution will reduce adsorption of lead onto soils. This adsorption is influenced by several factors such as the type and properties of adsorbent substances, pH, lead concentration and the type and concentration of other competing cations and complex forming inorganic and organic ligands [288].

### **3.9.4. Microbiological interactions**

The microbial and algal toxicity of lead has been utilized for two centuries to combat the fouling of ships' bottoms. However, some microorganisms have developed resistance mechanisms enabling them to grow in environments contaminated by lead. These mechanisms include bioaccumulation, bioadsorption and the precipitation of lead phosphates and lead sulphides [289, 290].

Conversely, microbial extracellular polymeric substances that are present in soils and in the soil pore waters are involved in soil–metal transport. Bacteria increase lead leaching and mineral dissolution owing to the secretion of organic molecules that can complex the lead ions in solution [291]. Studies of Sayer et al. [292] have shown the solubilization of the mineral  $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$  to hydrated lead and to oxalate via a reaction with organic acids produced by the fungus *Aspergillus niger*. In sediments, some bacteria of the genera

*Pseudomonas*, *Acinetobacter*, *Flavobacterium* and *Aeromonas* are able to transform lead nitrate and the trimethylated lead acetate into the lead tetramethyl [293]. All these processes serve to facilitate the solubilization of lead.

## **4. DATA AVAILABILITY AND UNCERTAINTY**

### **4.1. TYPES OF DATA AND ASSOCIATED UNCERTAINTIES**

The data needed to demonstrate confidence in MNA as a viable remediation option can be grouped into site specific and generic categories.

Site specific data are generated through characterization efforts and may already be available to an extent from sources such as geological surveys, meteorological and hydrological databases and previous environmental impact assessments. The availability of site data largely depends on the resources expended on the characterization effort.

Generic data include the thermochemical data that are discussed in Section 2.4 and which are not typically generated within individual remediation projects.

Uncertainties are inherent in any remediation activity and must be managed through a balance of uncertainty reduction (i.e. data collection) and uncertainty mitigation (e.g. use of monitoring data, probabilistic modelling) measures. Examples of pertinent uncertainties include [294]:

- (a) The exact nature of the acting transport and attenuation processes at the site and their variability over space and time;
- (b) The specific rates by which these transport and attenuation specific processes are operating;
- (c) The functional geometry of the site.

Uncertainty in MNA can only be effectively reduced and managed when it has been determined which uncertainties are significant. When significant uncertainties are identified, it can be decided whether to reduce these through data collection or to manage them through contingency planning.

#### **4.1.1. Site characterization**

Adequate site characterization is a fundamental requirement in any remediation project [7], but particularly when the MNA option is considered. As with many other remediation options, MNA requires the development of a site specific conceptual model and the measurement and demonstration of remediation performance. For MNA involving biologically mediated processes, the rates of transformation by which progeny are being formed need to be determined, while for MNA by heterogeneous reactions, the relevant adsorption or precipitation processes and possible interactions with other contaminants that may be beneficial or detrimental need to be identified. The challenge in site characterization is to demonstrate that beneficial processes do actually occur, to delineate relevant site properties in sufficient detail over the entire domain and to derive reassurance that the assumed processes will be sustained for a sufficient period of time. Site characterization, therefore, comprises a set of complementary elements [7, 25]:

- (a) Historical groundwater and/or soil chemistry data that demonstrate a clear and meaningful trend of decreasing contaminant mass and/or concentration over time at appropriate monitoring or sampling points.
- (b) Hydrogeological and geochemical data that can be used to demonstrate indirectly the types of natural attenuation process active at the site and the rates at which such processes will reduce contaminant concentrations to required levels. For example, characterization data may be used to quantify the rates of contaminant sorption, dilution and volatilization, or to demonstrate and quantify the rates of biological degradation processes occurring at the site.
- (c) Data from field or microcosm studies (conducted in or with actual contaminated site media) that directly demonstrate the occurrence of a particular natural attenuation process at the site and its capacity to attenuate the contaminants of concern.

Such characterization for MNA is discussed in more detail elsewhere [7, 25].

## **4.2. GENERIC CHEMICAL DATABASES**

#### **4.2.1. Thermodynamic databases**

Problems with the lack of consistency in thermodynamic databases were highlighted in the international CHEMVAL project [295], where an attempt

was made to achieve consensus on both data entry and *modus operandi* used in modelling procedures. Some progress was made towards this goal but, unfortunately, in the ten years since the project ended the situation has once again regressed with the creation of ever more and frequently disparate listings. Van der Lee and Lomenech [296] present a methodology for establishing a common 'operational' database but their work is still at an early stage. For this reason, it is prudent to verify safety critical calculations by comparing the output of two and preferably more databases.

Notwithstanding the above, for a small number of radiologically significant elements the picture is far brighter following the establishment of the ambitious OECD/NEA TDB project in 1984 [71]. This project sought to obtain critical reviews for those elements felt to be of particular importance for the safety assessment of radioactive waste disposal systems, but the resulting compilations have limited practical applicability as already discussed in Section 3. Twenty years on, four review reports have been published dealing with the chemical thermodynamics of uranium [161], americium [180], technetium [237], neptunium and plutonium [204]. An additional report published in 2003 [168] provides an update as the original reviews were already thought to be out of date. Radionuclide-bearing phases are included together with the properties of auxiliary phases (120 aqueous complexes, 95 solid phases and 65 gases). Uncertainties in  $\Delta G^\circ_f$ ,  $\Delta H^\circ_f$ ,  $S^\circ_f$  and  $C_p$  are given. The documents are generally regarded as the most authoritative guides to the aqueous chemistry of these elements and have been adopted by database compilers in many countries. For example, the HATCHES database [164], which is distributed by the OECD/NEA, incorporates the findings of the TDB project in combination with constants for the more common ions found in groundwaters.

Nuclear waste management national agencies have been sponsoring the compilation of databases, most notably HATCHES for NIREX Ltd [164, 297], NAGRA/PSI for the Nationale Genossenschaft für Radioaktiver Abfälle [298] and the JNC thermodynamic database for the Japan Nuclear Corporation [299]. These compilations draw heavily on the OECD/NEA work on radionuclides and on other data from the Lawrence Livermore National Laboratory (LLNL) [220]. The LLNL database itself is based on the SUPCRT95 database [300], whose core in turn is based on the work of Helgeson et al. [301]. This work has been extended in terms of aqueous species by Sverjensky et al. [302] and Shock et al. [303]. Unfortunately, the new aqueous species have not been implemented in the LLNL database. An overview of available compilations is given in Appendices I and II.

As discussed above, the OECD/NEA review of uranium thermodynamics [161], which is generally considered to be the most authoritative yet undertaken, did not originally include mineral phases owing to the perceived

lack of published experimental determinations of thermodynamic properties. This has been rectified to an extent in subsequent reviews [168, 180] from which the strengths and shortcomings in the available data are clear. The most complete set is that for oxide–hydroxide phases, reflecting the interest in spent fuel dissolution, and this is followed by that for the phosphates, among the most abundant group of secondary U(VI) phases. Very few attributable values exist for the corresponding silicates, arsenates, carbonates or sulphates. This is an area where further experimental work is obviously required.

The situation for the transuranic elements, which do not occur naturally, is less clear since there is no historical geochemical experience to draw on. Nevertheless, there is every indication that they will display geochemical behaviour that is similar in many respects, depending on oxidation state, to the lanthanides, uranium and thorium. In addition to new experimental data describing the incorporation of these elements into mineral phases, the need for reliable methods of estimating thermodynamic values is readily apparent. The same considerations apply to fission products such as technetium, though in this case the high mobility of the pertechnetate ion suggests that specific binding to certain classes of organic compound is the most likely means of retention in the near surface environment.

The suitability of speciation and coupled chemistry transport code for application to a given natural system depends not the least on the thermodynamic database used together with the code [295]. The contents of published databases naturally reflect the problem for which they were originally designed and often address only particular aspects, e.g. solids' properties [304]. A common problem is the lack of internal consistency, namely the data have not been corrected by the same methods for effects of experimental conditions, such as ionic strength, and have often not employed the same basic assumptions, such as species present. The problem is compounded by the lack of reference to the sources of the data in some of the databases that come with well-known speciation codes, such as PHREEQC2 [305]. When available, references are often only references to other databases [300]. Worse still, some databases also refer to data estimation results or to 'written communication'. Appendices I and II give an overview of available databases and their content.

Special care needs to be exercised by modellers when choosing a thermodynamic database for a particular problem in hand. Selection of an appropriate database will aid in reducing the uncertainty in modelling results. For further information, reference should be made to the following three documents:

- (1) The database comparison exercise by Price and Ross [306]. Criteria for database quality evaluation are given and applied to five thermodynamic databases.

- (2) An OECD/NEA report on this subject [307]. This report is the result of a collaboration involving 11 international organizations and aimed at an evaluation of thermodynamic databases against the requirements for their use in the context of nuclear waste disposal performance assessment.
- (3) Activities within the EU fuel cycle programmes [308].

#### **4.2.2. Kinetic data**

The limitations of equilibrium thermodynamics when applied to geochemical systems are well known. Whether a given system will attain equilibrium depends not only upon reaction kinetics but also on the physical properties of the porous medium. These properties determine the rate at which constituents can be transported to and from the reactive zone. Where reactions are fast relative to transport processes (e.g. diffusion), local equilibrium can often be assumed. However, heterogeneous reactions, particularly those involving dissolution of crystalline mineral solids are generally much slower than those in solution and the local equilibrium assumption is less valid. Such reactions can only be studied experimentally at elevated temperatures where phase transformations may occur and, further, the degree of order will have a significant effect on the Gibbs free energy. For most mineral phases the state of order is not known as a function of temperature or, in some cases, even at reference conditions.

Notwithstanding the difficulties outlined above, thermodynamic methods are inherently more defensible in an assessment context than a purely empirical approach. They can be used to identify at least those chemical reactions that are theoretically possible should equilibrium ultimately be attained. Even where the release of a given radionuclide from a matrix is kinetically controlled, for example the oxidative dissolution of uranium dioxide, its concentration in solution may be determined by the solubility of secondary phases that are amenable to thermodynamic treatment.

Chemical reaction kinetics are not commonly taken into account in performance assessment modelling. Low temperature reaction kinetics data have come mainly from basic geochemical studies into weathering phenomena and concern pure phases such as quartz, calcite and feldspars. Madé [309] and Jacquot [310], for instance, have compiled experimental data on dissolution and precipitation of quartz, calcite, dolomite, muscovite, kaolinite, illite, albite and (K-feldspar).

Kinetics may also play an important role in determining apparent or transient equilibria in other heterogeneous reactions, such as sorption. As discussed in Section 2.4.5, the macroscopic phenomenon of sorption may, on



the microscopic level, be a complex, multistep process, with some of the steps being kinetically controlled. Thus, with time a transformation of mobile/exchangeable form to a less mobile non-exchangeable form may occur as a result of diffusion into mineral lattice interlayers. Often these kinetics are described as a first order chemical reaction [257]. However, this approach may not be accurate enough over longer timescales. A ‘diffusion’ model proposed by Bulgakov and Konoplev [311] may overcome this problem.

Kinetic studies on the dissolution of radionuclide-bearing solid phases are sparse. The dispersion of fuel particles following the Windscale and Chernobyl incidents in the 1950s and 1980s, respectively, offered the opportunity to study their environmental behaviour, in particular their leaching behaviour. In the context of geological disposal of spent fuel and high level waste, various investigations into the kinetics of dissolution and transformation processes have been undertaken. However, the environmental conditions in this case are rather different from the near surface conditions under consideration here.

It has been shown with data for fuel particles released during the Chernobyl accident that their dissolution in soils can be satisfactorily described by first order kinetics [312–314]. Depending on the direction from the power plant the dissolution rate varied from 0.09/a towards the west to 0.27/a in other directions. The reason for slower dissolution of the fuel particles in the westerly direction was the lower oxidation level of uranium in the fuel matrix. These particles were formed as a result of the initial explosion at a relatively low temperature. Particles formed later, in conditions of the reactor fire, were more oxidized and correspondingly less resistant to dissolution. The controlling environmental parameter was found to be the soil pH [314, 315]. At pH values lower than 7, the rate of dissolution is faster than at pH values above 7, which also reflects the overall solubility of uranium as determined by the predominant carbonate species.

#### **4.2.3. Sorption data**

The discussion in Section 2.4.5.2 illustrates the problems faced by researchers attempting to quantify retardation of migrating radioactive species. Although there is a large body of sorption data available in the literature, it is of uneven quality and often of limited utility in performance assessments. In addition to dissimilarities in the conditions under which the measurements were made, there is as yet no universally agreed approach to modelling surface adsorption.

The OECD/NEA made a concerted effort to achieve a consensus via its ISIRS  $K_d$  database some 20 years ago and it still maintains an international working group in this field [71]. A comparable initiative focusing on surface

complexation modelling was launched more recently at the Forschungszentrum Rossendorf, Germany [316]. The listing, termed 'RES<sup>3</sup>T', was examined as part of this review and may constitute a useful tool as its development proceeds.

The theoretical concepts behind equilibrium sorption 'constants' have been critically discussed in Section 2.4.5.2.  $K_d$  values are apparent constants, which means that they depend on solution composition, solid/solution ratios, temperature and a whole range of properties (e.g. grain size distribution, specific surface area) of the solids concerned. This means that in theory all these parameters would be given in a  $K_d$  value database. Currently, two major compilations of  $K_d$  values are available. The first one, published by Chery and Sanjuan [317], describes Am, Cs, I, Ni, Np, Pu, Se, Sn, Th, Tc, U, Zr sorption on three different media (granite, sand and clay). Where available, solution composition, particle size, cation exchange capacity, specific surface area, experiment duration, solution volume and solid mass are given. The second major compilation of  $K_d$  values was published by the USEPA [112] for Cr, Cs, Pb, Pu, Ra, Sr, Th, U and tritium on media similar to those used in Ref. [317]. Cation exchange capacity, specific surface area, clay percentage, final pH and solution partial composition are also given.

Notwithstanding the theoretical reservations there may be towards the  $K_d$  concept, it finds widespread application in radioecological studies and some major compilations of respective data are available through this area of research [318, 319].

#### **4.2.4. Ion exchange**

Data for ion exchange are similarly scattered across a large number of publications in the earth sciences and agriculture (Table 5). Early compilations include those of Benson [320] and Maes and Cremers [321]. In an interesting development, a cation exchange model was applied to explain the variation in soil and stream water composition at the catchment scale in southern Norway [322]. This study serves to highlight the need for macroscopic descriptions of contaminant retention in addition to the microscopic and nanoscopic techniques currently being pursued.

#### **4.2.5. Surface complexation**

Again, data for surface complexation are scattered across a very large number of publications from different areas of research. There are not many specific surface complexation databases in the literature. Owing to the diversity of surface complexation models and to the natural variability of the parameter

TABLE 5. PUBLISHED DATA SETS WITH ION EXCHANGE DATA

Database	Solid material	Convention	Experimental conditions, remarks	Cations
Bruggenwert and Kamphorst [323]	Soils, clay minerals (smectites, illite, kaolinite, vermiculite)	Several explicit	Not fully detailed Some data at 75°C	Major and minor cations
Benson [324]	Smectites	Gapon	No Some data at 50°, 60° and 90°C	Na, Rb, K, Li, NH <sub>4</sub> , H, Fe (II), Ba, Co (II), Ni (II), Cu (II), Zn, Cd, Ca, Sr, Mg, Cs
Maes and Cremers [325]	Smectite, vermiculite, illite, interstratified illite/smectite, zeolites	Gaines and Thomas (not explicit)	Fews details Data at 25°C	Li, Na, K, Rb, Cs, Ca, Cu, Ag, Ni, Zn, Cd, Hg, organic molecules
Fletcher and Sposito [102]	Montmorillonite	Vanselow (not explicit)	No Data at 25°C	NH <sub>4</sub> , Na, H, K, Li, Ca, Mg, Sr, Cu, Zn, Cd, Co, Ni, CaCl, MgCl, SrCl, BaCl, CuCl, ZnNO <sub>3</sub> , CdNO <sub>3</sub> , CoCl, NiCl

values used (e.g. amorphous versus well-crystallized mineral specific surface area) this lack of established databases is not surprising.

In fact, the Dzombak and Morel database [326] is widely used but it should not be applied to complexation models other than the double layer model developed by the authors. Besides, this database only deals with sorption on iron oxyhydroxide. Twelve cations (Pb, Zn, Cd, Hg, Cu, Ag, Ni, Co, Cr, Ca, Sr and Ba) and 9 anions (PO<sub>4</sub>, AsO<sub>4</sub>, VO<sub>4</sub>, AsO<sub>3</sub>, BO<sub>3</sub>, SO<sub>4</sub>, SeO<sub>4</sub>, S<sub>2</sub>O<sub>3</sub> and CrO<sub>4</sub>) are tabulated, excluding any natural radionuclide.

### 4.3. PARAMETER ESTIMATION METHODS

Data estimation methods for aqueous and solid phases are needed since no thermodynamic data compilation can ever be complete. The majority of databases used for geochemical calculations contain only formation constants ( $\log \beta$ ) and solubility products ( $K_{sp}$ ) at 25°C for aqueous species and mineral solids, respectively. Numerous approaches have been developed over the past 15 years for estimating these constants where no suitable experimental data are available. These methods are based on correlations between ions having similar charge–size characteristics and the same or similar configuration of valence electrons [327].

Thus, empirical rules have been devised, describing the relative affinities between various donor ligands and metal ions, providing a guide to the likely stability constants for complexes where no direct experimental determinations are available [66]. The approaches are distinguished by the empirical relationships employed and the relative weighting attached to complexation affinities with various ligands. In addition, structural information on the preferred geometry of a metal ion with different ligands in binary or ternary configurations provides a means of estimating the stoichiometry of postulated complexes in multicomponent systems. Finally, a reasonable assessment of likely behaviour may be made by simple chemical analogy without recourse to complex algorithms. For example, the behaviour of actinide (III) ions such as  $\text{Am}^{3+}$  can be inferred from the properties of the corresponding lanthanides, neodymium and samarium. The use of chemical analogy as applied to the actinide elements is discussed in more detail by Moriyami et al. [328].

In the case of solids, data estimation relies heavily on structural information, for it has been shown that approximately linear relationships exist between molar volumes and entropy for many isostructural compounds [301]. Departures from this ideal behaviour have been attributed to crystal field effects for which corrections can be applied [329]. More recent hybrid approaches combine the above with statistical theory. Thus, many of the thermodynamic properties and functions required for estimating phase equilibria can be derived from basic principles and several ‘internally consistent’ data sets exist [330]. The two most commonly used are those of Berman [331] and Holland and Powell [332]. The different philosophies behind these compilations have been reviewed by Gottschalk [333].

The above methods have gained widespread acceptance in the geochemical community but have rarely been applied to radiologically important elements in waste disposal or problems associated with radioactive contamination. This is an essential aspect if emphasis is to shift from the collection of empirical ‘sorption’ data to a more fundamental appraisal of trace

element immobilization in rock–water systems coupled with a thermodynamic representation of the processes taking place.

## **5. ASSESSING THE POTENTIAL OF MNA**

### **5.1. MODELLING APPROACHES AND TOOLS**

#### **5.1.1. Introduction**

Models for MNA are of two main types: conceptual and numerical. The first comprises a set of interrelated hypotheses, which describe all or part of the system. Where these relate to the evolution of the system they have been termed ‘scenarios’, i.e. a postulated sequence of future events. Each makes assumptions about the initial and boundary conditions together with changes in physical and chemical properties with time. The strength or quality of the argument depends on consistency in the use of assumptions throughout the exercise. This gives confidence that the conclusions drawn can be justified by the information presented and not biased towards any given or desired outcome.

Mathematical models by contrast are quantitative expressions of a conceptual model, comprising a set of algebraic, differential and/or integral equations, and rely on numerical data. The primary requirement is for traceability to ensure that interpretations are based on sound evidence. Reports on the results derived from such models need to include an indication of the level of confidence or uncertainty associated with the output. Data transfer between models and any processing or adjustments made to experimental values should be transparent. Finally, not all of the data required for a safety assessment are amenable to measurement. The methods by which values are estimated, whether by formal data elicitation techniques or otherwise, should also be apparent to the reviewer.

#### **5.1.2. Geochemical calculation codes**

Garrels and Thompson [334] are widely regarded as the founders of geochemical modelling. Since then, numerous codes have been developed to calculate the chemical speciation of solutions in equilibrium with solid phases and reactive surfaces. Among these, PHREEQC [305], EQ3/6 [220] and

MINTEQA2 [335] are the most commonly used. Other examples include GEOCHEMIST'S WORKBENCH<sup>®</sup> [336], GEMS [336, 337] and CHESS [338]. Though all of these tools solve the same basic equations, each has advantages in terms of functionality. For example, EQ3/6 can exploit Pitzer's approach to calculate ion activities (where data permit) and is therefore suitable for modelling systems with high salt concentrations. PHREEQC is generally regarded as easier to use and perhaps more suitable for simulating surface complexation phenomena. Table 6 [339] compares the functionality of three of the codes mentioned above.

### 5.1.3. Coupled geochemistry–transport codes

The simulation of reactive contaminant transport requires an adequate understanding of both chemical and hydrogeological processes acting in tandem. This is not provided by the large number of 'radionuclide transport models' described in the literature that invoke the diffusion–dispersion equation and a somewhat cursory approach to chemical interactions (e.g. the distribution coefficient,  $K_d$ ) to account for retardation. The dominant chemical factors likely to influence aqueous radionuclide migration include: speciation, both organic and inorganic; precipitation and dissolution; sorption/exchange and diffusion in response to chemical gradients. To these must be added colloid dispersion and flocculation, though the impact of these ultra-fine particulates is not yet fully understood. If the vadose zone is to be modelled, a three phase (gas/aqueous/solid) model is needed. In sparsely fractured rock, a model assuming homogeneous, laminar flow would not be adequate. Such coupling poses a challenge to numerical solution methods; however, the main challenge is achieving a satisfactory parameterization of the system. In recent years, considerable effort has been devoted towards developing coupled geochemistry transport codes. Appendix III summarizes the characteristics of some currently available tools.

This Section describes the basic concepts behind hydrogeochemical models and outlines some of the approaches used to couple hydrogeological transport to chemical equilibria. For a more exhaustive treatment the reader is referred to the early reviews of Rubin [340] and Mangold and Tsang [341]. Yeh and Tripathi [342] and Zysset et al. [343] also provide useful appraisals of the relative merits of alternative coupling strategies.

Mathematical representation of the transport of solutes by advection, diffusion and kinematic dispersion is governed by the conservation of mass, energy and charge. Rubin [340] describes alternative formulations of the basic solute transport equations and assesses their application to fast, reversible reactions as opposed to slow and/or irreversible reactions. This clear distinction

TABLE 6. PRINCIPAL CHARACTERISTICS OF PHREEQC, EQ3/6 AND MINTEQA2 [339]

Functionalities	PHREEQC2 [305]	EQ3/6 [220]	MINTEQA2 [335]
Reaction progress dependent calculation	Yes	Yes	No
Ion activity models	Extended Debye-Hückel, or Davies Pitzer (PHRQPITZ code, not including all PHREEQC functionalities)	Extended Debye-Hückel, Davies or Pitzer	Extended Debye-Hückel, or Davies
Redox reaction	Based on electron activity	Explicit definition of redox couples	Explicit definition of redox couples Based on electron activity
Solid solutions	Multiple ideal solid solutions Binary non-ideal solid solutions	Multiple ideal solid solutions Binary and ternary non-ideal solid solutions	No
Gaseous phases	Yes (fixed volumes or pressure)	Yes (fixed pressure)	Yes (fixed pressure)
Ion exchange	Yes	No	Yes
Surface complexation model	Double layer or no electrostatic models Explicit calculation of electrostatic layer composition	No	Double layer Triple layer model Explicit calculation of electrostatic layer composition
Isotopic fractionation	Yes	No	No
Kinetics	Yes	Yes	No
Equation solver	Newton-Raphson Based on equilibrium constants.	Newton-Raphson for speciation Taylor series Based on equilibrium constants	Global resolution method with one step. Constraint on mass balance. Newton-Raphson Based on equilibrium constants

defines the limits of applicability of the ‘local equilibrium assumption’ but, in practice, coupling inevitably involves a compromise. Until recently, limitations with respect to data availability and computer resources meant that reconciling the requirements of a large number of non-equilibrium reactions with a geometrically complex flow field was unrealistic. New developments in the computer sciences have now removed one of the obstacles to achieving significant enhancements in coupled chemical transport modelling, though the lack of high quality data for many radioactive contaminants remains a very real constraint.

Several coupled codes have been evaluated within the CHEMVAL project [295, 344]. The overwhelming majority simulate chemical systems at equilibrium subjected to a constant velocity flow in one or, rarely, two dimensions. They all address the ingress of a solution of known composition at the boundary (static or transient) into a field solution whose composition must also be specified a priori. The model then simulates the displacement of the initial solution by mixing and reaction with the boundary fluid.

Two distinct protocols for coupling chemical reactions to transport equations have been followed. The direct or ‘one step’ method [345–347] involves solving mass action equations representing the chemical system and transport terms simultaneously. The resulting codes suffer from numerical constraints owing to the ‘stiffness’ of the highly non-linear hybrid equations employed. Attempts to extend one step models by incorporating reaction kinetics [348, 349] have largely been abandoned.

By contrast, the indirect or two step method [342, 350] employs discrete chemical and non-reactive transport modules, performing iterations between these to ‘move’ the evolving solution in space and time. This approach is inherently more flexible and, in principle, can be extended to highly complex chemical systems and transport pathways. For these reasons, two step methods have largely superseded one step coupled models and are believed to offer the best prospects for hydrogeochemically demanding or resource intensive applications.

#### **5.1.4. Modelling biological effects**

Biological factors are difficult to incorporate satisfactorily into coupled models, owing to the dependence of reaction kinetics upon an enormous variety of site specific environmental conditions. Therefore, establishing a database that is applicable generally to biologically mediated processes is problematic. However, some recent studies have sought, with some degree of success, to couple microbial metabolism to redox changes and contaminant transport processes [351–354].



Irrespective of conditions or contaminant(s), the overwhelming majority of such models start from a set of common assumptions. These include the need for a source of carbon (substrate for reproduction), nutrients (such as nitrogen and phosphorus), electron acceptors (mainly oxygen, nitrate and sulphate) and appropriate conditions for bacterial growth (pH, temperature, etc.). The formation of a biofilm as both a separate phase and an interface between the solution and the solid is generally accepted though its geometry and properties are not yet fully understood [355]. The principal subject of contention is the rate at which diffusion through the biofilm occurs and whether or not this is reaction rate limiting.

Biological reactions have been simulated in a variety of ways that may be grouped into the following categories:

- (a) **Instantaneous reactions.** Where the rate of reaction is fast relative to groundwater velocity, local equilibrium may be assumed and very simple relationships employed to describe the fate of the contaminant plume [356]. Such models are unlikely to hold true in most natural systems, since even though attachment to surfaces may be reversible, the desorption step is normally slow in comparison.
- (b) **First order decay.** Biological reactions are treated in a manner analogous to radioactive decay [357]. The main advantage of this method is its simplicity; the main disadvantage, the absence of any mechanistic basis.
- (c) **Monod kinetics.** This describes the growth of bacterial cultures as a function of a limiting nutrient. The basic equation [358] has been modified by a number of workers over the years to incorporate additional controls [359]. The method is the most widely used at present but, in any case, the approach is purely empirical.
- (d) **Michaelis–Menton kinetics.** This differs from the above in its derivation from a mechanistic analysis of enzymic reactions. It is employed when the substrate is not regarded as a critical control on reaction progress [360]. Michaelis–Menton based analysis is the most complex of those listed here and has the most demanding data requirements.

A number of hybrid modelling approaches have been proposed that employ two or more of the above methods. For instance, Rifai et al. [356] describe a ‘generic’ code, BIOPLUME III, that offers a choice of models at different points along a given pathway; the latter being subdivided according to the dominant electron acceptor.

### **5.1.5. Airborne transport**

Models for airborne transport have seen considerable use in both routine and accidental release situations. These dispersion models vary considerably in approach and complexity according to requirements. It may be noted that models are only as accurate as the underlying conceptual model captures the situation in hand and as the quality and coverage of input data allows. The spatial scale of dispersion models can vary from a few hundred metres to a global scale. The essential mechanisms to be modelled in one way or another are the effects of advection by the actual or prevailing wind field, dispersion by turbulence and dry and/or wet deposition. In addition, resuspension processes, radioactive decay, heterogeneous chemical reactions and inputs from other sources may need to be considered [44]. Quantifying the source term, of course, is of critical importance. It will be necessary to specify the chemical and physical properties of the material released, the time dependency of the release, the total release for each species and the effective height above ground of the release.

### **5.1.6. Modelling food chain transfer**

Contrary to the models used for aqueous and airborne transport, which are largely mechanistic in nature, food chain and soil-to-plant transfer models are typically empirical or semi-empirical in nature [47]. Extensive use is made of default parameter values for various models, which can be found, for example, in Ref. [48]. The underlying reason for this seems to be that the most extensive use of them is being made in emergency situations, when there is no time to undertake a comprehensive site assessment.

In addition to the transport and transformation processes discussed in the previous sections, the following phenomena, processes and compartments can be involved in radionuclide transport through terrestrial and aquatic food chains to human receptors [47, 48]:

- (a) Dry or wet deposition onto the soil or plants;
- (b) Root uptake by plants;
- (c) Uptake through other plant tissues;
- (d) Translocation within plants to edible tissues;
- (e) Ingestion and skin uptake of aquatic animals;
- (f) Translocation of contaminants within animals into the meat or products, such as milk;
- (g) Adhesion of soil particles to plant surfaces;
- (h) Ingestion by humans of plant and animal tissues;

- (i) Ingestion of ground- and surface waters by animals and humans;
- (j) Direct ingestion of surface soil by humans and grazing animals;
- (k) Ingestion of soil particles adhering to plant surfaces by humans and grazing animals.

In addition to the above processes, food chain models sometimes include a more or less 'black box' treatment of:

- (a) Transfer of contaminants from catchment to water bodies;
- (b) Transfer of contaminants in surface water to the terrestrial system by spray irrigation;
- (c) Transfer of contaminants in surface water to bottom sediments.

However, some of these would be amenable to a more mechanistic treatment as outlined in the previous sections.

## 5.2. MONITORING

If natural attenuation has been accepted by the regulator as part of the remediation option, performance monitoring and contingency plans, respectively, are required to evaluate its long term effectiveness and to provide a fall back option should the solution fail. Monitoring requires the presence of institutional control and in itself is a form of institutional control [6, 12]. Monitoring is a significant and essential component of MNA and the programme would be designed to [27, 361, 362]:

- (a) Ensure that natural attenuation is occurring according to expectations;
- (b) Ensure that there is no impact to important receptors;
- (c) Detect any new releases of contaminants to the environment that could impact the effectiveness of the natural attenuation remedy;
- (d) Demonstrate the efficacy of institutional controls that have been put in place;
- (e) Detect any changes in the environmental conditions (e.g. hydrogeological, geochemical, microbiological) that would compromise the underlying conceptual site model and reduce the efficacy of any of the natural attenuation processes;
- (f) Verify compliance with the cleanup objectives.

In the past, techniques for the monitoring of dispersed radioactive contamination entailed semi-quantitative gross activity or dose measurements

taken on-site combined with sampling of soils, sediments and waters, as well as flora and fauna, for subsequent laboratory analysis. The difficulties of ensuring adequate coverage of the site and representative sampling are well documented in the literature. Recent developments in field analytical techniques allow quantitative and semi-quantitative in situ and on-site determination of a wide range of contaminants [7, 12, 13].

It should be noted that, ultimately, all remediation options that do not entail complete removal of the contaminant source would, de facto, revert to an 'MNA' scenario.

## **6. CONCLUDING DISCUSSION**

### **6.1. SCOPE, OPPORTUNITIES AND LIMITATIONS**

MNA is increasingly being considered a viable option for sites contaminated by biodegradable organic pollutants. To date, it has not received the same level of attention in the case of radioactively contaminated land, perhaps understandably given public concerns and strict regulatory controls on exposure to ionizing radiation. However, there are situations for which active remediation to levels of free release is not feasible, either because the source is inaccessible or the contamination is dispersed over a wide area [16]. Many former mining sites contain natural series nuclides at levels that are little more than background [5]. Similarly, the principal radionuclides in residues from a number of industrial processes are relatively short lived. Scales from natural gas wells, for example, are hazardous owing to the presence of  $^{210}\text{Pb}$  and  $^{210}\text{Po}$ . Such situations might well benefit from adoption of MNA. It could also serve as an interim approach, pending a decision on the final remediation strategy.

Regulators are necessarily cautious about approving the application of new technologies or procedures, particularly where the approach is regarded as 'unproven'. Thus, it is important to note that, although MNA is not formally considered an option for radioactive contamination at present, reliance on natural barriers to migration is the de facto method employed in many cases. A great deal of information that could be used in case studies is already available from failed containment systems (e.g. Hanford), nuclear accidents (Chernobyl), mine tailings and spoil heaps, etc.

The use of MNA as a remedial strategy is not equivalent to 'no action' and nor is it a 'walk away' option; monitoring implies a degree of institutional

control. Relying on natural processes does not abrogate responsibility for controlling the source of the contamination, preventing exposures or, ultimately, restoring the site to appropriate beneficial use if this is a requirement of the remediation. Social, cost and risk factors have to be considered before implementing any decision on cleanup [15]. A comprehensive characterization programme will invariably be required in order to develop an understanding of the attenuation processes operating at the site and their sustainability [7, 13]. Radiological and, where appropriate, other (e.g. toxicological) risk assessments will also be required [18]. Nevertheless, MNA offers several potential advantages over alternative remediation strategies, including potentially lower costs and lower occupational dose to site workers. It is also the least intrusive remediation option and does not depend on the availability of a secondary waste disposal site or waste transfers.

Thus, MNA implies a long term commitment to monitoring and the maintenance of institutional controls. More extensive education and outreach efforts may be required in order to gain public acceptance of MNA. These fall into the ambit of stewardship, an issue addressed in a companion report [17].

There are sites, contaminants and pollution situations, however, where MNA will not be applicable. Physical, chemical, hydrogeological and biological conditions may not allow attenuation to proceed at a sufficient rate to protect human and environmental receptors. Restrictions on land use and the vulnerability of key receptors also have to be taken into account. Other potential disadvantages of MNA include longer time-frames to achieve remediation objectives when compared to active measures and the potential for continued contaminant migration and/or cross-media transfer of contaminants. Hydrological and geochemical conditions may change over time and could result in renewed mobility of previously stabilized contaminants. This applies in particular to borderline cases (e.g. retention in natural wetlands) where small changes in environmental conditions may lead to a remobilization of the contaminants.

## 6.2. ENHANCING ATTENUATION

If MNA is demonstrated (e.g. by modelling or monitoring) as not being capable of achieving the desired levels of radionuclide retardation or exposure prevention, then the possibilities for enhancing the naturally present attenuation mechanisms can be explored. Contrary to other active measures this does not include any transfer of radionuclides into other media requiring subsequent handling and disposal *ex situ*, such as phytoremediation or constructed wetlands [16]. However, an unbiased discrimination between

‘active’ in situ remediation techniques and enhancement of attenuation cannot always be made. Enhancing attenuation involves the use of minimum invasive techniques to modify the physical, chemical or biological properties of the subsurface (soil, groundwater, aquifer matrix) in order to improve the conditions for natural attenuation processes. In the case of radionuclides, the stimulation of indigenous microorganisms will not lead to a metabolic destruction of contaminants, but can bring about their immobilization owing to alteration of redox conditions [363]. Thus, for example, the species  $\text{TcO}_4^-$  and  $\text{UO}_2^{2+}$ , which are stable under oxidizing conditions, can be transformed into insoluble reduced solids. In contrast, Pu(V) and Pu(VI) can be immobilized by sorption onto iron hydroxides, which, of course, are stable only under oxidizing conditions. In any case, attempts to enhance attenuation permanently requires a profound knowledge of the site specific geochemistry and its likely dynamics over the time-frame under consideration. Terms such as ‘irreversible sorption’ (e.g. for  $^{137}\text{Cs}$  ( $t_{1/2} = 30$  a) on clay minerals) need to be used carefully, as hydraulic and chemical conditions of groundwater bodies, particularly in industrialized environments, are subject to changes over timescales of decades.

Typical techniques to enhance attenuation and retardation in the subsurface include [16]:

- (a) Adjustment of desired redox conditions for precipitation of radionuclides;
- (b) Introduction of directly oxidizing (e.g. air,  $\text{O}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\text{KMnO}_4$  and various proprietary compositions) or reducing compounds ( $\text{Na}_2\text{SO}_3$ , sodium dithionite and various proprietary compositions);
- (c) Introduction of carbon sources (e.g. methanol, molasses), electron donors (e.g.  $\text{H}_2$ , lactate and various proprietary compounds) or electron acceptors (e.g.  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) to stimulate bacterial growth. Limited experience with regard to their application to radionuclides exists [364, 365];
- (d) Improvement of sorption capacity of the subsurface by adding colloidal sorbents (e.g. organic polymers, clay minerals, carbonates, phosphates, iron oxides/hydroxides).

Depending on the type and scale of the technical implementation, the necessary measures (injection wells, permeable reactive barriers) may be actually classified as ‘in situ remediation’.



**Appendix I**

**OVERVIEW OF PUBLISHED THERMOCHEMICAL DATASETS**

Name	Elements	Aqueous complexes	Gases	Minerals	References	DHr	log K 25°C	log K (T)	Volume
OECD/NEA TDB	45	120	65	95	Yes	Values in DH, DS and DCp	No	No	No
CHESS	47	625	10	639	No	No	Yes	Yes	No
NAGRA/PSI	40	320	6	85	Yes	Yes	Yes	Yes	No
Berman	12	0	4	67	Yes	Values in DH, DS and DCp	No	No	Yes
Chatterjee et al.	16	0	3	145	Yes	Values in DH, DS and DCp	No	No	No
CODATA	34	35	60	55	Yes	Yes	No	No	No
Gottschalk	12	0	3	91	Yes	Values in DH, DS and DCp	No	No	Yes
GRI-Mech	7	0	52	0	No	Values in DH, DS and DCp	No	No	No
Holland and Powell	15	22	6	142	Yes	Values in DH, DS and DCp	No	No	Yes
TDB JNC	42	415	75	585	Yes	Yes	Yes	No	No
LLNL GWB (EQ3/6)	81	1503	93	1122	Yes	Yes	Yes	Yes	Yes
SUPCRT92 (Slop98.dat)	37	1343	22	193	Yes	Yes	No	No	Yes
MINTEQA2	37	1100	13	525	No	Yes	Yes	Yes	No
PHREEQC	24	179	8	47	No	Yes	Yes	Yes	No
WATEQ4F	33	380	8	329	No	Yes	Yes	Yes	No
HATCHES	65	1282	6	912	Yes	Yes	Yes	Yes	Yes
Robie and Hemingway	50	28	9	443	Yes	Values in DH, DS and DCp	No	No	Yes
Naumov et al.	84	500	0	1700	Yes	Values in DH, DS and DCp	No	No	Yes
Phillips et al.	52	630	85	730	Yes	Values in DH, DS and DCp	No	No	No
Wagman et al.	103	14 300 substances			No	Values in DH, DS and DCp	No	No	No



## Appendix II

## ADDITIONAL DETAILS OF PUBLISHED THERMOCHEMICAL DATASETS

Name	Consistency	Reference	URL
OECD/NEA TDB	Critical evaluation	[71]	<a href="http://www.nea.fr">http://www.nea.fr</a>
CHES	No	[338]	<a href="http://chess.enscm.fr/databases.html">http://chess.enscm.fr/databases.html</a>
NAGRA/PSI	Critical	[298]	<a href="http://les.web.psi.ch/TDBbook/">http://les.web.psi.ch/TDBbook/</a>
Berman 1988	Yes	[331]	<a href="http://www.gis.nrcan.gc.ca/twq.html">http://www.gis.nrcan.gc.ca/twq.html</a>
Chatterjee et al.	Yes	[366]	<a href="http://www.uni-bayreuth.de/departments/math/org/mathe7/OLBRICHT/software/Bayes/Bayes.htm">http://www.uni-bayreuth.de/departments/math/org/mathe7/OLBRICHT/software/Bayes/Bayes.htm</a>
CODATA	Yes	[367]	<a href="http://www.codata.org/databases/key1.html">http://www.codata.org/databases/key1.html</a>
Gottschalk	Yes	[333]	<a href="http://www.gfz-potsdam.de/pb4/pg1/dataset/index.html">http://www.gfz-potsdam.de/pb4/pg1/dataset/index.html</a>
GRL-Mech	No	[368]	<a href="http://www.me.berkeley.edu/gri_mech/data/thermo_table.html">http://www.me.berkeley.edu/gri_mech/data/thermo_table.html</a>
Holland and Powell	Yes	[332]	<a href="http://www.esc.cam.ac.uk/astaff/holland/thermocalc.html">http://www.esc.cam.ac.uk/astaff/holland/thermocalc.html</a>
TDB JNC	Critical evaluation	[299]	<a href="http://migrationdb.jnc.go.jp/english.html">http://migrationdb.jnc.go.jp/english.html</a>
LLNL GWB (EQ3/6)	No	[220]	<a href="http://www.geology.uiuc.edu/Hydrogeology/hydro_thermo.htm">http://www.geology.uiuc.edu/Hydrogeology/hydro_thermo.htm</a>
SUPCRT92 (Slop98.dat)	Yes	[300]	<a href="http://geopig.asu.edu/supert92_data/slop98.dat">http://geopig.asu.edu/supert92_data/slop98.dat</a>
MINTEQA2	No	[335]	<a href="http://www.geology.uiuc.edu/Hydrogeology/hydro_thermo.htm">http://www.geology.uiuc.edu/Hydrogeology/hydro_thermo.htm</a>
PHREEQC	No	[305]	<a href="http://www.geology.uiuc.edu/Hydrogeology/hydro_thermo.htm">http://www.geology.uiuc.edu/Hydrogeology/hydro_thermo.htm</a>
WATEQ4F	No	[369]	<a href="http://water.usgs.gov/software/wateq4f.html">http://water.usgs.gov/software/wateq4f.html</a>
HATCHES	Critical evaluation	[164, 297]	<a href="http://www.sercoassurance.com/ea/weg_chem.htm">http://www.sercoassurance.com/ea/weg_chem.htm</a>
Robie and Hemingway	Critical evaluation	[304]	n/a
Naumov et al.	Critical evaluation	[370]	n/a
Phillips et al.	Critical evaluation	[371]	n/a
Wagman et al.	Critical evaluation	[372]	n/a

**Appendix III**

**PRINCIPAL CHARACTERISTICS OF COUPLED GEOCHEMISTRY-TRANSPORT CODES**

Codes	Coupling	Calcu- lational scheme	Dimen- sion	NZS	Porosity changes	Kinetics	Redox	Ion exchange	Surface comp- lexation	Heat transfer	Parallel	URL
PHAST	Iterative	Finite differences	3-D	No	No	Yes	Yes	Yes	Yes	No	Yes	<a href="http://www.brr.cr.usgs.gov/projects/GWC_coupled/phast/index.html">http://www.brr.cr.usgs.gov/ projects/GWC_coupled/ phast/index.html</a>
HGBC123D	Particle tracking	Finite differences	3-D	No	No	Yes	Yes	Yes	Yes	Yes	Yes	<a href="http://hbgc.esd.ornl.gov/">http://hbgc.esd.ornl.gov/</a>
UTCHEM	No, iterative	Centered Finite differences	3-D	Yes	Yes	No	No	Yes	Yes	Yes	No	<a href="http://www.epa.gov/ada/csmos/models/utchem.html">http://www.epa.gov/ada/ csmos/models/utchem.html</a>
HYTEC	Iterative	Finite volumes	2-D	Yes	Yes	Yes	Yes	Yes	Yes	No	Yes	<a href="http://hytec.ensmp.fr/">http://hytec.ensmp.fr/</a>
TOUGH- REACT	Iterative	Finite differences Integration	3-D	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	<a href="http://www-esd.lbl.gov/TOUGHREACT/">http://www-esd.lbl.gov/ TOUGHREACT/</a>
CHEM- TOUGH	Implicit	Finite differences Integration	3-D	Yes	Yes	Yes	?	No	No	Yes	No	No
NUFT	?	Finite differences	3-D	Yes	Yes	Yes	Yes	No	No	Yes	Yes	<a href="http://www.llnl.gov/CAFDA/Glassley/glassley.html">http://www.llnl.gov/ CAFDA/Glassley/ glassley.html</a>
FLOTTRAN	Implicit	Finite differences	3-D	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	?

# **PRINCIPAL CHARACTERISTICS OF COUPLED GEOCHEMISTRY –TRANSPORT CODES (cont.)**

Codes	Coupling	Calculational scheme	Dimension	NZS	Porosity changes	Kinetics	Redox	Ion exchange	Surface complexation	Heat transfer	Parallel	URL
CRUNCH	Implicit/iterative	Finite volumes	3-D	Yes	Yes	Yes	Yes	Yes	Yes	No	Yes	<a href="http://www.pnl.gov/cse/subsurface/crunch.htm">http://www.pnl.gov/cse/subsurface/crunch.htm</a>
PHT3D	Iterative	Several schemes	3-D	No	No	Yes	Yes	Yes	Yes	No	No	<a href="http://www.pht3d.org/">http://www.pht3d.org/</a>

## REFERENCES

- [1] INTERNATIONAL ATOMIC ENERGY AGENCY, Management of Radioactive Waste from the Mining and Milling of Ores, Safety Standards Series No. WS-G-1.2, IAEA, Vienna (2002).
- [2] INTERNATIONAL ATOMIC ENERGY AGENCY, Factors for Formulating Strategies for Environmental Restoration, IAEA-TECDOC-1032, IAEA, Vienna (1998).
- [3] INTERNATIONAL ATOMIC ENERGY AGENCY, A Directory of Information Resources on Radioactive Waste Management, Decontamination and Decommissioning, and Environmental Restoration, Data as of June 1995, IAEA-TECDOC-841, IAEA, Vienna (1995).
- [4] INTERNATIONAL ATOMIC ENERGY AGENCY, Technologies for Remediation of Radioactively Contaminated Sites, IAEA-TECDOC-1086, IAEA, Vienna (1999).
- [5] INTERNATIONAL ATOMIC ENERGY AGENCY, Extent of Environmental Contamination by Naturally Occurring Radioactive Material (NORM) and Technological Options for Mitigation, Technical Reports Series No. 419, IAEA, Vienna (2003).
- [6] INTERNATIONAL ATOMIC ENERGY AGENCY, Monitoring and Surveillance of Residues from the Mining and Milling of Uranium and Thorium, Safety Reports Series No. 27, IAEA, Vienna (2002).
- [7] INTERNATIONAL ATOMIC ENERGY AGENCY, Characterization of Radioactively Contaminated Sites for Remediation Purposes, IAEA-TECDOC-1017, IAEA, Vienna (1998).
- [8] INTERNATIONAL ATOMIC ENERGY AGENCY, Design Criteria for a Worldwide Directory of Radioactively Contaminated Sites (DRCS), IAEA-TECDOC-1251, IAEA, Vienna (2001).
- [9] INTERNATIONAL ATOMIC ENERGY AGENCY, Technical Options for the Remediation of Contaminated Groundwater, IAEA-TECDOC-1088, IAEA, Vienna (1999).
- [10] INTERNATIONAL ATOMIC ENERGY AGENCY, The Long Term Stabilization of Uranium Mill Tailings, IAEA-TECDOC-1403, IAEA, Vienna (2004).
- [11] INTERNATIONAL ATOMIC ENERGY AGENCY, Remediation of Areas Contaminated by Past Activities and Accidents, Safety Standards Series No. WS-R-3, IAEA, Vienna (2003).
- [12] INTERNATIONAL ATOMIC ENERGY AGENCY, Compliance Monitoring for Remediated Sites, IAEA-TECDOC-1118, IAEA, Vienna (1999).
- [13] INTERNATIONAL ATOMIC ENERGY AGENCY, Site Characterization Techniques Used in Environmental Restoration Activities, IAEA-TECDOC-1148, IAEA, Vienna (2000).

- [14] INTERNATIONAL ATOMIC ENERGY AGENCY, Release of Sites from Regulatory Control on Termination of Practices, IAEA Safety Standards Series No. WS-G-2.8, IAEA, Vienna (in preparation).
- [15] INTERNATIONAL ATOMIC ENERGY AGENCY, Non-technical Factors Impacting on the Decision Making Processes in Environmental Remediation, IAEA-TECDOC-1279, IAEA, Vienna (2002).
- [16] INTERNATIONAL ATOMIC ENERGY AGENCY, Remediation of Sites with Dispersed Radioactive Contamination, Technical Reports Series No. 424, IAEA, Vienna (2004).
- [17] INTERNATIONAL ATOMIC ENERGY AGENCY, Management of Long Term Radiological Liabilities: Stewardship Challenges, IAEA, Vienna (in preparation).
- [18] INTERNATIONAL ATOMIC ENERGY AGENCY, Remediation of Sites with Mixed Contamination of Radioactive and Other Hazardous Substances, Technical Reports Series No. 442, IAEA, Vienna (2005).
- [19] INTERNATIONAL ATOMIC ENERGY AGENCY, Radiation Legacy of the 20th Century: Environmental Restoration, IAEA-TECDOC-1280, IAEA, Vienna (2002).
- [20] UNITED STATES NATIONAL RESEARCH COUNCIL, Natural Attenuation for Groundwater Remediation, Committee on Intrinsic Remediation, National Academies Press, Washington, DC (2000).
- [21] NETWORK FOR INDUSTRIALLY CONTAMINATED LAND IN EUROPE (NICOLE), Project: Natural Attenuation: Guidelines for Acceptance, <http://www.nicole.org>
- [22] FORSCHUNGSZENTRUM JÜLICH/FORSCHUNGSZENTRUM KARLSRUHE, KORA – Kontrollierter natürlicher Rückhalt und Abbau von Schadstoffen bei der Sanierung kontaminierter Grundwässer und Böden, <http://www.natural-attenuation.de>
- [23] UNITED STATES ENVIRONMENTAL PROTECTION AGENCY, Symposium on Natural Attenuation of Ground Water, Rep. EPA/540/R-97/504, USEPA, Corvallis, OR (1997).
- [24] AMERICAN SOCIETY FOR TESTING AND MATERIALS, Guide for Remediation by Natural Attenuation, ASTM-E 1943-98, ASTM, Philadelphia, PA (1998).
- [25] SANDIA NATURAL ATTENUATION PROJECT, <http://www.sandia.gov/eesector/gc/gc/snap.html>
- [26] SWINDOLL, M., STAHL, R.G., Jr., ELLS, S.J. (Eds.), Natural Remediation of Environmental Contaminants: Its Role in Ecological Risk Assessment and Risk Management, <http://www.seatac.org>
- [27] UNITED STATES ENVIRONMENTAL PROTECTION AGENCY, Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites, OSWER Directive 9200.4-17P, USEPA, Washington, DC (1999).

- [28] UNITED STATES ENVIRONMENTAL PROTECTION AGENCY, Natural Attenuation of Hexavalent Chromium in Groundwater and Soils, Rep. EPA/540/S-94/505, USEPA, Washington, DC (1994).
- [29] INTERNATIONAL ATOMIC ENERGY AGENCY, The International Chernobyl Project: An Overview, Report by an International Advisory Committee, Technical Report, IAEA, Vienna (1991).
- [30] INTERNATIONAL ATOMIC ENERGY AGENCY, Guidelines for Agricultural Countermeasures Following an Accidental Release of Radionuclides, Technical Reports Series No. 363, IAEA, Vienna (1994).
- [31] MILLER, W., Potential Natural Safety Indicators and Their Application to Radioactive Waste Disposal in the UK, Rep. 6297A-1, Version 2, NIREX, Harwell, OX (2000).
- [32] VAGANOV, P., The Use of Selected Safety Indicators (Concentrations, Fluxes) in the Assessment of Radioactive Waste Disposal: Dispersion Halos and Fluxes of Chemical Elements in Permafrost or Periglacial Regions, Nuclear Waste Disposal Rep. YST-107, Geol. Surv. Finland, Espoo (2002).
- [33] NUCLEAR WASTE MANAGEMENT ORGANIZATION OF JAPAN, Development of Repository Concepts for Volunteer Siting Environment, Rep. NUMO-TR-04-03, NUMO, Tokyo (2004).
- [34] ATOMIC ENERGY OF CANADA LIMITED, Summary of the Environmental Impact Statement on the Concept for Disposal of Canada's Nuclear Fuel Waste, Rep. AECL-10721, COG-93-11, AECL, Pinawa, MB (1994) 47.
- [35] MONITORED NATURAL ATTENUATION WEB RESOURCES, <http://www.gw-mna.com>
- [36] GOLIAN, S., ERDMAN, J., DAWSON, G., BRADY, P.V., RICE, D., BLACK, P., The Department of Energy's Monitored Natural Attenuation Initiative (2000), <http://www.wmsym.org/wm2000/pdf/29/29-7.pdf>
- [37] UNITED STATES DEPARTMENT OF ENERGY, Technical Guidance for the Long-term Monitoring of Natural Attenuation Remedies at Department of Energy Sites (1999), <http://www.em.doe.gov/techguide/techguide.pdf>
- [38] YEH, G.T., SALVAGE, K.M., GWO, J.P., ZACHARA, J.M., SZECSDY, J.E., HYDROBIOGEOCHEM: A Coupled Model of HYDROlogic Transport and Mixed BIOGEOCHEMical Kinetic/Equilibrium Reactions in Saturated – Unsaturated Media, Rep. ORNL/TM-13668, Oak Ridge Natl Lab., TN (1998).
- [39] ZHU, M., et al., "A three-dimensional numerical model for the evaluation of intrinsic biodegradation and remedial actions at groundwater-contaminated sites near Los Angeles, California", ICEM '97 Radioactive Waste Management and Environmental Remediation (Proc. 6th Int. Conf. Singapore, 1997), ASME, New York (1997) 645–654.
- [40] IVANOVICH, M., HARMON, R.S. (Eds.), Uranium-series Disequilibrium: Applications to Earth, Marine and Environmental Sciences, Clarendon Press, Oxford (1992).
- [41] MAIDMENT, D.R. (Ed.), Handbook of Hydrology, McGraw-Hill, Inc., New York (1992).

- [42] WORLD METEOROLOGICAL ORGANIZATION, Hydrological Aspects of Accidental Pollution of Water Bodies, WMO Operational Hydrology Rep. No. 37, WMO, Geneva (1992) 208.
- [43] BRADY, P.V., et al., “Soil radionuclide plumes”, *Geochemistry of Soil Radionuclides* (ZHANG, P.C., BRADY, P.V., Eds), Soil Sci. Soc. Am. Spec. **59** (2002).
- [44] VAN DER STRICHT, E., KIRCHMANN, R. (Eds), *Radioecology: Radioactivity and Ecosystems*, Fortemps, Liège, Belgium (2001).
- [45] WARNER, F., HARRISON R.M. (Eds), “Radioecology after Chernobyl: Biogeochemical Pathways of Artificial Radionuclides”, *SCOPE 50*, John Wiley, New York (1993) 367.
- [46] INTERNATIONAL ATOMIC ENERGY AGENCY, *Atmospheric Dispersion in Nuclear Power Plant Siting*, Safety Series No. 50-SG-S3, IAEA, Vienna (1980).
- [47] INTERNATIONAL ATOMIC ENERGY AGENCY, *Generic Models for Use in Assessing the Impact of Discharges of Radioactive Substances to the Environment*, Safety Reports Series No. 19, IAEA, Vienna (2001).
- [48] INTERNATIONAL ATOMIC ENERGY AGENCY, *Handbook of Parameter Values for the Prediction of Radionuclide Transfer in Temperate Environments*, Technical Reports Series No. 364, IAEA, Vienna (1994).
- [49] FETTER, C.W., *Contaminant Hydrogeology*, Prentice Hall, Upper Saddle River, NJ (1999) 500 pp.
- [50] HADLEY, R.F., et al., “Recent developments in erosion and sediment yield studies”, *Technical Documents in Hydrology, IHP-II Project A.1.3.1*, UNESCO, Paris (1985) 128.
- [51] BERNER, R.A., *Early Diagenesis – A Theoretical Approach*, Princeton University Press, Princeton, NJ (1980).
- [52] BORZILOV, V.A., et al., Experimental research of radionuclide wash-off after the Chernobyl accident, *Soviet Meteorology and Hydrology* **11** (1988) 43–53 (in Russian).
- [53] INTERNATIONAL ATOMIC ENERGY AGENCY, *Sediments and Pollution in Waterways: General Considerations*, IAEA-TECDOC-302, IAEA, Vienna (1984) 185 pp.
- [54] HSÜ, K.J., *Physics of Sedimentology – Textbook and Reference*, 2nd edn, Springer, Berlin (2004).
- [55] HARVEY, R.W., GARBEDIAN, S.P., Use of colloid filtration theory in modeling movement of bacteria through a contaminated sandy aquifer, *Environ. Sci. Technol.* **25** (1991) 175–185.
- [56] CHANT, L.A., et al.,  $^{129}\text{I}$  and  $^{36}\text{Cl}$  concentrations in lichens collected in 1990 from three regions around Chernobyl, *Appl. Radiat. Isot.* **47** 9–10 (1996) 933–937.
- [57] BOSTOCK, A.C., SHAW, G., BELL, J.N.B., The volatilisation and sorption of I-129 in coniferous forest, grassland and frozen soils, *J. Environ. Radioact.* **70** 1–2 (2003) 29–42.
- [58] HIRNER, A.V., et al., Metal(loid) organic compounds in geothermal gases and waters, *Org. Geochem.* **29** (1998) 1765–1778.

- [59] BOLZE, C.E., MALONE, P.G., SMITH, M.J., Microbial mobilization of barite, *Chem. Geol.* **13** (1974) 141–143.
- [60] LAROCK, P., et al., Bacterial mobilization of polonium, *Geochim. Cosmochim. Acta* **60** 22 (1996) 4321–4328.
- [61] MOMOSHIMA, N., et al., Formation and emission of volatile polonium compounds by microbial activity and polonium methylation with methylcobalamin, *Environ. Sci. Technol.* **35** (2001) 2956–2960.
- [62] MOMOSHIMA, N., et al., Biologically induced Po emission from fresh water, *J. Environ. Radioact.* **63** 2 (2002) 187–197.
- [63] INTERNATIONAL ATOMIC ENERGY AGENCY, Measurement and Calculation of Radon Releases from Uranium Mill Tailings, Technical Reports Series No. 333, IAEA, Vienna (1992).
- [64] FERRY, C., et al., Radon exhalation from uranium mill tailings: Experimental validation of a 1-D model, *J. Environ. Radioact.* **54** 1 (2001) 99–108.
- [65] HOLLANDER, W., GARGER, E. (Eds), Contamination of Surfaces by Resuspended Material, ECP-1 Final Report, Rep. EUR 16527EN, Office for Official Publications of the European Communities, Luxembourg (1996).
- [66] ALLARD, B., et al., Modelling in Aqueous Chemistry, OECD, Paris (1997).
- [67] MELCHIOR, D., BASSETT, R., Chemical modelling of aqueous systems II, *ACS Symp. Ser.* **416** (1990).
- [68] OZIABKIN, V.N., “Modelling the transport of contaminants through groundwater flow systems: Reactive chemical transport”, paper presented at Int. Sem. on Environmental Modelling, Jurmala, Latvia, 1995.
- [69] PARKHURST, D., THORSTENSON, D., PLUMMER, L., PHREEQE: A Computer Program for Geochemical Calculations, Rep. WRI-80-96, US Geological Survey, Denver, CO (1985).
- [70] FALCK, W.E., READ, D., THOMAS, J., CHEMVAL 2: Thermodynamic Database, Rep. EUR 16897, Office for Official Publications of the European Communities, Luxembourg (1996).
- [71] OECD NUCLEAR ENERGY AGENCY, Thermochemical Database Project (TDB) (2004), <http://www.nea.fr/html/dbtdb/info/publications/welcome.html>
- [72] UNITED STATES ENVIRONMENTAL PROTECTION AGENCY, Recent Developments for In Situ Treatment of Metal Contaminated Soils, Rep. EPA/542/R-97/004, USEPA, Washington, DC (1997).
- [73] SCHILK, A.J., et al., The Role of Organic Complexants and Microparticulates in the Facilitated Transport of Radionuclides, Rep. NUREG/CR-6429, Nuclear Regulatory Commission, Washington, DC (1996).
- [74] URBAN, N.R., et al., Mobility and diagenesis of Pb and <sup>210</sup>Pb in peat, *Geochim. Cosmochim. Acta* **54** (1990) 3329–3346.
- [75] BOYLE, R.W., Cupriferous bogs in the Sackville area, New Brunswick, Canada, *J. Geochem. Explor.* **8** (1977) 495–528.



- [76] GARDEA-TORRESDEY, J.L., TANG, L., SALVADOR, J.M., "Copper adsorption by Sphagnum peat moss and its different humic fractions", 10th Annual Conf. on Hazardous Waste Research, Kansas City (1995), <http://www.engg.ksu.edu/HSRC/95Proceed/tang.html>
- [77] FIRSOVA, E.V., GERMAN, K.E., PERETROUKHIN, V.F., KHIJNYAK, T.V., "Bioaccumulation of long-lived radionuclides by fresh-water silt", Environmental Contamination in Central and Eastern Europe (Proc. 4th Int. Symp. Warsaw, 1998), Institute for International Cooperative and Environmental Research, Tallahassee, FL (1998).
- [78] READ, D., FALCK, W.E., "Long-term uranium migration behaviour: An overview of the 'natural analogue' studies carried out on the British Isles", Uranium Mining and Hydrogeology (Proc. Int. Symp. Freiberg, 1995), Sven von Loga, Cologne (1995) 473–482.
- [79] HAIGH, D., et al., The Effect of Organics on the Sorption of Strontium, Caesium, Iodine, Neptunium, Uranium and Europium by Glacial Sand, Rep. WE/89/16, British Geological Survey, Keyworth, UK (1989) 36.
- [80] FALCK, W.E., HOOKER, P.J., "Quantitative Interpretation of Halogen Porewater Concentration Profiles in Lake Sediments", Scientific Basis for Nuclear Waste Management XIV (Proc. Symp. Boston, 1990), Materials Research Society, Pittsburgh, PA (1990) 757–764.
- [81] BRAUN, J.-J., et al., Mobilization and redistribution of REEs and thorium in a syenitic lateritic profile: A mass balance study, *Geochim. Cosmochim. Acta* **57** (1993) 4419–4434.
- [82] EYAL, Y., OLANDER, D., Leaching of uranium and thorium from monazite: I. Initial leaching, *Geochim. Cosmochim. Acta* **54** (1990) 1867–1877.
- [83] READ, D., et al., The degradation of monazite: Implications for the mobility of rare earth and actinide elements during low temperature alteration, *Eur. J. Mineral.* **14** (2002) 487–498.
- [84] HELGESON, H., AAGAARD, P., Activity composition relations among silicates and aqueous solutions: 1. Thermodynamics of intrasite mixing and substitutional order/disorder in minerals, *Am. J. Sci.* **285** (1985) 769–844.
- [85] PUTNIS, A., FERNANDEZ-DIAZ, L., PRIETO, M., Experimentally produced oscillatory zoning in the (Ba,Sr)SO<sub>4</sub> solid solution, *Nature* **358** (1992) 743–745.
- [86] WARING, C.L., TAYLOR, J.R., "A new technique for building in-situ subsurface hydrologic barriers: NBT", Mine, Water and Environment (Proc. Int. Symp. Seville, 1999), International Mine Water Association (1999) 663–665.
- [87] ZIEGENBALG, G., "In-situ remediation of heavy metal contaminated soil or rock formations and sealing of water inflows by directed and controlled crystallization of natural occurring minerals", Mine, Water and Environment (Proc. Int. Symp. Seville, 1999), International Mine Water Association (1999) 667–672.
- [88] DACHEUX, N., et al., Actinide immobilisation in new matrices based on solid solutions: Th<sub>4-x</sub>M<sub>x</sub><sup>IV</sup>(PO<sub>4</sub>)P<sub>2</sub>O<sub>7</sub> (M<sup>IV</sup>= <sup>238</sup>U, <sup>239</sup>Pu), *J. Alloys Compounds* **271–273** (1998) 236–239.

- [89] BRUNO, J., SANDINO, A., The thermodynamics and kinetics of co-precipitation and its effect on radionuclide solubility, *Radiochim. Acta* **44/45** (1988) 17–21.
- [90] GORDON, L., SALUTSKY, M., WILLARD, H., “Co-precipitation from homogeneous solutions”, *Precipitation from Homogeneous Solutions*, John Wiley, New York (1959).
- [91] DOERNER, H., HOSKINS, W., Co-precipitation of radium and barium sulphates, *Am. Chem. Soc.* **46** (1925) 662–675.
- [92] LIPPMANN, F., Stable and metastable solubility diagrams for the system  $\text{CaCO}_3\text{-MgCO}_3\text{-H}_2\text{O}$  at ordinary temperature, *Bull. Mineral.* **105** (1982) 273–279.
- [93] PRIETO, M., et al., Nucleation, growth and zoning phenomena in crystallising  $(\text{Ba,Sr})\text{CO}_3$ ,  $(\text{Ba,Sr})\text{SO}_4$  and  $(\text{Cd,Ca})\text{CO}_3$  solid solutions from aqueous solutions, *Geochim. Cosmochim. Acta* **61** (1997) 3383–3397.
- [94] CECCARELLO, S., et al., Suppression of radium uptake in barite crystals by introduction of competing ions, *Min. Eng.* **17** (2004) 323–330.
- [95] DZOMBAK, D., MOREL, F., *Surface Complexation Modelling: Hydrous Ferric Hydroxide*, John Wiley, New York (1990).
- [96] STUMM, W. (Ed.), *Aquatic Surface Chemistry*, John Wiley, New York (1987) 520 pp.
- [97] TURNER, D.R., PABALAN, R.T., BERTETTI, F.P., Neptunium V sorption on montmorillonite: An experimental and surface complexation modeling study, *Clay Minerals* **46** (1998) 256–267.
- [98] AKCAY, H., Aqueous speciation and pH effect on the sorption behavior of uranium by montmorillonite, *J. Radioanal. Nucl. Chem.* **237** 1–2 (1998) 133–137.
- [99] MCKINLEY, J.P., et al., The influence of uranyl hydrolysis and multiple site-binding reactions on adsorption of U(VI) to montmorillonite, *Clays Clay Miner.* **43** 5 (1995) 586–598.
- [100] STAUNTON, S., ROUBAUD, M., Adsorption of  $^{137}\text{Cs}$  on montmorillonite and illite: Effect of charge compensating cation, ionic strength, concentration of Cs, K and fulvic acid, *Clays Clay Miner.* **45** 2 (1997) 251–260.
- [101] ABUSAF, A., YÜCEL, H., Removal of  $^{137}\text{Cs}$  from aqueous solutions using different cationic forms of a natural zeolite: Clinoptilolite, *Sep. Purif. Technol.* **28** 2 (2002) 103–116.
- [102] FLETCHER, P., SPOSITO, G., The chemical modeling of clay/electrolyte interactions for montmorillonite, *Clay Miner.* **24** (1989) 375–391.
- [103] MAHONEY, J.J., LANGMUIR, D., Adsorption of Sr on kaolinite, illite and montmorillonite at high ionic strengths, *Radiochim. Acta* **54** (1991) 139–144.
- [104] SCHLEGEL, M., et al., Adsorption mechanisms of Zn on hectorite as a function of time, pH, and ionic strength, *Am. J. Sci.* **301** (2001) 798–830.
- [105] SCHLEGEL, M., et al., Sorption of metal ions on clay minerals: III. Nucleation and epitaxial growth of Zn phyllosilicates on the edges of hectorite, *Geochim. Cosmochim. Acta* **65** (2001) 4155–4470.
- [106] FREUNDLICH, H., *Colloid and Capillary Chemistry*, Methuen, London (1926).
- [107] MCKEE, S., SWAILES, D., On the derivation of the Langmuir isotherm for adsorption kinetics, *J. Phys., A Math. Gen.* **24** (1991) 207–209.

- [108] BROWN, J., Kudzu as a medium for adsorption of heavy metals in dilute aqueous waste streams, *Pra. J. Haz. Toxic Radioact. Waste* **4** (2000) 82–87.
- [109] KINNIBURGH, D., General purpose adsorption isotherms, *Environ. Sci. Technol.* **20** (1986) 895–904.
- [110] McKINLEY, I., SCHOLTIS, A., “A comparison of radionuclide sorption databases used in recent performance assessments”, (Proc. OECD/NEA Sorption Workshop Interlaken, 1991), OECD, Paris (1991).
- [111] OECD NUCLEAR ENERGY AGENCY, “Chemical modelling of sorption in the field of radioactive waste management”, (Proc. Int. Workshop Oxford, 1997), OECD, Paris (1997).
- [112] UNITED STATES ENVIRONMENTAL PROTECTION AGENCY, Understanding Variation on Partition Coefficient,  $K_d$ , Values: II. Review of Geochemistry and Available  $K_d$  Values for Cadmium, Caesium, Chromium, Lead, Plutonium, Radon, Strontium, Thorium, Tritium ( $^3\text{H}$ ) and Uranium, Rep. 402-R-99-004B, USEPA, Washington, DC (1999).
- [113] JAMES, R., PARKS, G., Characterisation of aqueous colloids by their electrical double layer and intrinsic surface chemical properties, *Surf. Colloid. Sci.* **12** (1982) 119–216.
- [114] HOHL, H., STUMM, W., Interaction of  $\text{Pb}^{2+}$  with hydrous  $\alpha\text{-Al}_2\text{O}_3$ , *J. Colloid Interface Sci.* **55** (1976) 281–288.
- [115] STUMM, W., HUANG, C., JENKINS, S., Specific chemical interactions affecting the stability of dispersed systems, *Croat. Chem. Acta* **42** (1970) 223–244.
- [116] DAVIS, J., KENT, D., “Surface complexation modelling in aqueous geochemistry”, *Mineral–Water Interface Chemistry* (HOCELLA, M., WHITE, A., Eds), *Rev. Mineral.* **23** (1990) 177–260.
- [117] BRADBURY, M.H., BAEYENS, B., A mechanistic description of Ni and Zn sorption on Na-montmorillonite Part II: Modeling, *J. Contam. Hydrol.* **27** (1997) 223–248.
- [118] McCARTHY, J.F., ZACHARA, J.M., Subsurface transport of contaminants, *Environ. Sci. Technol.* **23** 5 (1998).
- [119] HIEMENZ, P.C., *Principles of Colloid and Surface Chemistry*, 2nd edn, Marcel Dekker, New York (1986).
- [120] KIM, J.I., Actinide colloids in natural aquifer systems, *MRS Bull.* **19** 12 (1994) 47–53.
- [121] RYAN, J.N., ELIMELECH, M., Review: Colloid mobilization and transport in groundwater, *Colloids Surf.* **107** A (1996) 1–56.
- [122] DENEUX-MUSTIN, S., et al., *Mobilité et transfert racinaire des éléments en traces, influence des micro-organismes du sol*, Edition Tec et Doc, Paris (2003).
- [123] CHARLET, L., LIGER, E., GERASIMO, P., Decontamination of TCE- and U-rich waters by granular iron: Role of sorbed  $\text{Fe(II)}$ , *J. Environ. Eng.* **124** (1998) 25–30.
- [124] MADIGAN, M.T., MARTINKO, J.M., PARKER, J., *Brock’s Biology of Microorganisms*, Prentice Hall, Upper Saddle River, NJ (2000).

- [125] WADE, Z.J., DICHRISTINA, T.J., Isolation of U<sup>VI</sup> reduction-deficient mutants of *Shewanella putrefaciens*, FEMS Microbiol. Lett. **184** (2000) 143–148.
- [126] LLOYD, J.R., et al., Technetium reduction and precipitation by sulfate-reducing bacteria, Geomicrobiol. J. **15** (1998) 43–56.
- [127] RUSIN, P.A., et al., Solubilization of plutonium hydrous oxide by iron-reducing bacteria, Environ. Sci. Technol. **28** (1994) 1686–1690.
- [128] HAAS, J.R., DICHRISTINA, T.J., WADE, R., Thermodynamics of U(VI) sorption onto *Shewanella putrefaciens*, Chem. Geol. **180** (2001) 33–54.
- [129] LIGER, E., CHARLET, L., VAN CAPPELLEN, P., Surface catalysis of uranium(VI) reduction by iron(II), Geochim. Cosmochim. Acta **63** 19/20 2939–2956.
- [130] O'LOUGHLIN, E.J., et al., “Investigation of the transformation of uranium under iron-reducing conditions: Reduction of U(VI) by biogenic Fe(II)/Fe(III) hydroxide (green rust)”, paper presented at USDOE-NABIR PI Workshop, Warrenton, 2004.
- [131] BEYENAL, H., et al., Uranium immobilization by sulfate-reducing biofilms, Environ. Sci. Technol. **38** 7 (2004) 2067–2074.
- [132] LOJOU, E., BIANCO, P.J., Electrocatalytic reduction of uranium by bacterial cytochromes: Biochemical and chemical factors influencing the catalytic process, J. Electroanal. Chem. **471** (1999) 96–104.
- [133] PAYNE, R.B., et al., Uranium reduction by *desulfovibrio desulfuricans* strain G20 and a cytochrome *c*<sub>3</sub> mutant, Appl. Environ. Microbiol. **68** 6 (2002) 3129–3132.
- [134] FEIN, J.B., et al., A chemical equilibrium model for metal adsorption onto bacterial surfaces, Geochim. Cosmochim. Acta **61** 16 (1997) 3319–3328.
- [135] STRANDBERG, G.W., SHUMATE II, S.E., PAROTT, J.R., Jr., Microbial cells as biosorbents for heavy metals: Accumulation of uranium by *Saccharomyces cerevisiae* and *Pseudomonas aeruginosa*, Appl. Environ. Microbiol. **41** (1981) 237–245.
- [136] LLOYD, J.R., YONG, P., MACASKIE, L.E., Biological reduction and removal of Np(V) by two micro-organisms, Environ. Sci. Technol. **34** 7 (2000) 1297–1301.
- [137] TSEZOS, M., VOLESKY, B., The mechanisms of thorium biosorption, Biotechnol. Bioeng. **24** (1982) 955–969.
- [138] GADD, G.M., WHITE, C., “Heavy metal and radionuclide accumulation and toxicity in fungi and yeasts”, Metal-Microbe Interactions (POOLE, R.K., GADD, G.M., Eds), IRL Press, Oxford (1989) 19–38.
- [139] YONG, P., MACASKIE, L.E., Removal of lanthanum, uranium and thorium from the citrate complexes by immobilized cells of *Citrobacter sp.* in a flow-through reactor : Implications for the decontamination of solutions containing plutonium, Biotechnol. Lett. **19** (1997) 251–256.
- [140] BERTHELIN, J., MUNIER-LAMY, C., Microbial mobilization and preconcentration of uranium from various rock materials by fungi, Environ. Biogeochem. **35** (1983) 395–401.

- [141] ANDRES, Y., MacCORDICK, H.J., HUBERT, J.C., Bacterial biosorption and retention of thorium and uranyl cations by *Mycobacterium smegmatis*, J. Radioanal. Nucl. Chem. **166** (1992) 431–440.
- [142] TURNER, J.S., ROBINSON, N.J., Cyanobacterial metallothioneins: Biochemistry and molecular genetics, J. Ind. Microbiol. **14** (1995) 119–125.
- [143] JEONG, B.C., et al., Localization of enzymatically enhanced heavy metal accumulation by *Citrobacter sp.* and metal accumulation in vitro by liposomes containing entrapped enzyme, Microbiology **143** (1997) 2497–2507.
- [144] MARQUES, A.M., et al., Uranium accumulation by *Pseudomonas sp.* EPS-5028, Appl. Microbiol. Biotechnol. **35** (1991) 406–410.
- [145] PREMIZIC, E.T., et al., Induced formation of chelating agents by *Pseudomonas aeruginosa* grown in the presence of thorium and uranium, Arch. Environ. Contam. Toxicol. **14** (1985) 759–768.
- [146] AMACHI, S., et al., Bacteria mediate methylation of iodine in marine and terrestrial environments, Appl. Environ. Microbiol. **67** 6 (2001) 2718–2722.
- [147] AMACHI, S., et al., Microbial participation in iodine volatilization from soils, Environ. Sci. Technol. **37** (2003) 3885–3890.
- [148] RAUSER, W.E., Phytochelatins and related peptides (structure, biosynthesis, and function), Plant Physiol. **109** (1995) 1141–1149.
- [149] DIELS, L., et al., The *czc* operon of *Alcaligenes eutrophus* CH34: From resistance mechanism to the removal of heavy metals, J. Ind. Microbiol. **14** (1995) 142–153.
- [150] MACASKIE, L.E., et al., Uranium bioaccumulation by a *Citrobacter sp.* as a result of enzymically-mediated growth of polycrystalline  $\text{HUO}_2\text{PO}_4$ , Science **257** (1992) 782–784.
- [151] BARNES, L.J., et al., A new process for the microbial removal of sulphate and heavy metal from contaminated waters extracted by a geohydrological control system, Chem. Eng. Res. Des., **69A** (1991) 184–186.
- [152] KRAVETS, A.P., “Biological control of the radionuclides migration into system soil–plant and new methods for soil restoration”, Environmental Contamination in Central and Eastern Europe (Proc. 4th Int. Symp. Warsaw, 1998), Institute for International Cooperative and Environmental Research, Tallahassee, FL (1998).
- [153] SALOMONS, W., FÖRSTNER, U. (Eds), Chemistry and Biology of Solid Waste: Dredged Material and Mine Tailings, Springer, New York (1988).
- [154] GONZÁLES, A.J., Radioactive residues of the Cold War period: A radiological legacy, IAEA Bull. **40** 4 (1998) 2–11.
- [155] WARNER, F., HARRISON, R. (Eds), Radioecology after Chernobyl: Biogeochemical Pathways of Artificial Radionuclides, John Wiley, New York (1993).
- [156] MILLER, W., et al., Natural analogue studies in the geological disposal of radioactive wastes, Stud. Environ. Sci. **57** (1994).
- [157] WERME, L.O., SPAHIU, K., Direct disposal of spent nuclear fuel: Comparison between experimental and modelled actinide solubilities in natural waters, J. Alloys and Compounds **271–273** (1998) 194–200.

- [158] NATIONALE GENOSSENSCHAFT FÜR DIE LAGERUNG RADIOAKTIVER ABFÄLLE, “Nukleare Entsorgung Schweiz — Konzept und Realisierungsplan”, NAGRA Tech. Rep. NTB-92-02, NAGRA, Baden, Switzerland (1992).
- [159] KATZ, J., SEABORG, G., MORSS, L., The Chemistry of the Actinide Elements, Chapman and Hall, London (1986).
- [160] GMELIN, L., Handbuch der anorganischen Chemie, Suppl. Ser., Uranium, Springer, Heidelberg (1979).
- [161] GRENTHE, I., et al., Chemical Thermodynamics Series: Volume 1. Chemical Thermodynamics of Uranium, North-Holland, Amsterdam (1992).
- [162] IVANOVICH, M., HARMON, R., Uranium Series Disequilibrium: Applications to Earth, Marine and Environmental Sciences, Clarendon, Oxford (1992).
- [163] READ, D., HOOKER, P., Using data from natural geochemical environments to improve models of uranium speciation in groundwaters, *J. Geochem. Explor.* **46** (1992) 63–81.
- [164] NIREX, HATCHES, Version 16, OECD/NEA Release, OECD, Paris (2004).
- [165] BAES, C., MESMER, R., The Hydrolysis of Cations, John Wiley, New York (1976).
- [166] MOSKVIN, A., SHELYAKINA, A., PERMINOV, P., Solubility product of uranyl phosphate and the composition and dissociation constants of uranyl phosphato-complexes, *Russ. J. Inorg. Chem.* **12** (1967) 1756–1760.
- [167] DONGARRA, G., LANGMUIR, D., The stability of  $\text{UO}_2\text{OH}^+$  and  $\text{UO}_2[\text{HPO}_4]_2^{2-}$  complexes at 25°C, *Geochim. Cosmochim. Acta* **44** (1980) 1747–1751.
- [168] GUILLAUMONT, R., et al., Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium, Elsevier, Amsterdam (2003).
- [169] CLARK, D., HOBART, D., NEU, M., Actinide carbonate complexes and their importance in actinide environmental chemistry, *Chem. Rev.* **95** (1995) 25–48.
- [170] NIKOLAEVA, N., The study of hydrolysis and complexing of uranyl ions in sulphate solutions at elevated temperatures, *Izv. Sib. Otd. Akad. Nauk. SSSR* (1971) 62–66 (in Russian).
- [171] READ, D., et al., “Natural uranium fluxes and their use in repository safety assessment”, Uranium in the Aquatic Environment (MERKEL B., PLANER-FRIEDRICH, B., WOLKERSDORFER, C., Eds), Springer, Heidelberg (2002) 115–126.
- [172] INTERNATIONAL ATOMIC ENERGY AGENCY, Uranium Extraction Technology, Technical Reports Series No. 359, IAEA, Vienna (1994).
- [173] INTERNATIONAL ATOMIC ENERGY AGENCY, Manual of Acid In Situ Leach Uranium Mining Technology, IAEA-TECDOC-1239, IAEA, Vienna (2001).
- [174] KIM, J., The chemical behaviour of transuranium elements and barrier functions in natural aquifer systems, *Mater. Res. Soc. Symp. Proc.* **294** (1993) 3–21.

- [175] READ, D., et al., The migration of uranium into peat-rich soils at Broubster, Caithness, Scotland, *J. Contam. Hydrol.* **13** (1993) 291–308.
- [176] MANDARINO, J., *Fleischer's Glossary of Mineral Species*, Mineralogical Record, Tucson, AZ (1999).
- [177] BURNS, P.C., FINCH, R. (Eds), *Uranium — Mineralogy, Geochemistry and the Environment*, *Reviews in Mineralogy* **38**, Mineralogical Society of America, Chantilly, VA (1999).
- [178] FORSYTH, R., WERME, L., Spent fuel corrosion and dissolution, *J. Nucl. Mater.* **190** (1992) 3–19.
- [179] TRUEMAN, E., et al., Alteration of depleted uranium metal, *Geochim. Cosmochim. Acta* **67** (2003) A493.
- [180] SILVA, R.J., et al., *Chemical Thermodynamics of Americium*, Elsevier, Amsterdam (1995).
- [181] HSI, C.-K., LANGMUIR, D., Adsorption of uranyl onto ferric oxyhydroxides: Application of the surface complexation site-binding model, *Geochim. Cosmochim. Acta* **49** (1985) 1931–1941.
- [182] WAITE, T., et al., Uranium(VI) adsorption to ferrihydrite: Application of a surface complexation model, *Geochim. Cosmochim. Acta* **24** (1994) 5465–5478.
- [183] PAYNE, T., et al., Surface complexation model of uranyl sorption on Georgia kaolinite, *Appl. Clay Sci.* (2004) 151–162.
- [184] STAMBERG, K., VENKATESAN, K., VASUDEVA RAO, P., Surface complexation modelling of uranyl ion sorption on mesoporous silica, *Colloids Surf.* **221** (2003) 149–162.
- [185] SHANBAG, P., CHOPPIN, G., Binding of uranyl by humic acid, *J. Inorg. Nucl. Chem.* **43** (1981) 3369–3372.
- [186] READ, D., HOOKER P., “The speciation of uranium and thorium at the Broubster natural analogue site, Caithness, Scotland”, *Scientific Basis for Nuclear Waste Management XII* (Proc. Symp. Boston, 1988), Materials Research Society, Pittsburgh, PA (1989) 763–770.
- [187] READ, D., ROSS, D., SIMS, R., The migration of uranium through Clashach sandstone: The role of low molecular weight organics in enhancing radionuclide transport, *J. Contam. Hydrol.* **35** (1998) 235–248.
- [188] MISSANA, T., GARCIA-GUTIERREZ, M., MAFFIOTTE, C., Experimental and modelling study of the uranium(VI) sorption on goethite, *J. Colloid Interface Sci.* **260** (2003) 291–301.
- [189] MISSANA, T., GARCIA-GUTIERREZ, M., FERNANDEZ, V., Uranium(VI) sorption on colloidal magnetite under anoxic environment: Experimental study and surface complexation modelling, *Geochim. Cosmochim. Acta* **67** (2003) 2543–2550.
- [190] BRUNO, J., et al., Experimental study and modelling of the U(VI)–Fe(OH)<sub>3</sub> surface precipitation/co-precipitation equilibria, *Geochim. Cosmochim. Acta* **59** (1995) 4113–4123.



- [191] DUFF, M., URBANIK-COUGHLIN, J., HUNTER, D., Uranium co-precipitation with iron oxide minerals, *Geochim. Cosmochim. Acta* **66** (2002) 3533–3547.
- [192] MURAKAMI, T., et al., Mobility of uranium during weathering, *Am. Mineral.* **82** (1997) 888–899.
- [193] LENHART, J., HONEYMAN, B., Uranium(VI) sorption to hematite in the presence of humic acid, *Geochim. Cosmochim. Acta* **63** (1999) 2891–2901.
- [194] LOVLEY, D.R., Dissimilatory Fe(III) and Mn(IV) reduction, *Microbiol. Rev.* **55** (1991) 529–587.
- [195] LOVLEY, D.R., Dissimilatory metal reduction, *Annu. Rev. Microbiol.* **47** (1993) 263–90.
- [196] LOVLEY, D.R., PHILLIPS, E.J.P., Reduction of uranium by *Desulfovibrio desulfuricans*, *Appl. Environ. Microbiol.* **58** (1992) 850–856.
- [197] TEBO, B.M., OBRAZTSOVA, A.Y., Sulfate-reducing bacterium grows with Cr(VI), U(VI), Mn(VI) and Fe(III) as electron acceptors, *FEMS Microbiol. Lett.* **162** (1998) 193–198.
- [198] PIETZSCH, K., HARD, B.C., BABEL, W., A *Desulfovibrio* sp. capable of growing by reducing U(VI), *J. Basic. Microbiol.* **39** (1999) 365–372.
- [199] LLOYD, J.R., Microbial reduction of metals and radionuclides, *FEMS Microbiol. Rev.* **27** (2003) 411–425.
- [200] ANDERSON, R.F., et al., Uranium deposition in Saanich Inlet sediments, Vancouver Island, *Geochim. Cosmochim. Acta* **53** (1989) 2205–2213.
- [201] KLIMKHANNER, G.P., PALMER, M.R., Uranium in the oceans: Where it goes and why?, *Geochim. Cosmochim. Acta* **55** (1991) 1799–1806.
- [202] SELENSKA-PROBELL, et al., “Bacterial communities in uranium mining waste piles and their interaction with heavy metals”, *Uranium in the Aquatic Environment* (MERKEL, B., PLANER-FRIEDRICH, B., WOLKERSDORFER, C., Eds), Springer, Heidelberg (2002) 455–465.
- [203] MERROUN, M., et al., “Characterization of uranium (VI) complexes formed by different bacteria relevant to uranium mining waste piles”, *ibid.*, p. 505–511.
- [204] LEMIRE, R., et al., *Chemical Thermodynamics of Neptunium and Plutonium*, Elsevier, Amsterdam (2001).
- [205] MOSKVIN, A., ESSEN, L., BUKHTIYAROVA, T., The formation of thorium (IV) and uranium (IV) complexes in phosphate solutions, *Russ. J. Inorg. Chem.* **12** (1967) 1794–1795 (in Russian ).
- [206] NECK, V., RUNDE, W., KIM, J., Solid–liquid equilibria of neptunium(V) in carbonate solutions of different ionic strengths: II. Stability of the solid phases, *J. Alloys Compounds* **225** (1995) 295–302.
- [207] NECK, V., FANGHÄNEL, T., KIM, J., Mixed hydroxo-carbonate complexes of neptunium(V), *Radiochim. Acta* **77** (1997) 167–175.
- [208] CHOPPIN, G., Speciation of trivalent f elements in natural waters, *J. Less-Common Met.* **126** (1986) 307–313.
- [209] CHOPPIN, G., Soluble rare earth and actinide species in seawater, *Mar. Chem.* **28** (1986) 19–26.



- [210] ERIKSEN, T.E., et al., Solubility of the Redox Sensitive Radionuclides  $^{99}\text{Tc}$  and  $^{237}\text{Np}$  Under Reducing Conditions in Neutral to Alkaline Solutions: Effect of Carbonate, SKB Rep. TR-93-18, SKB, Stockholm (1992).
- [211] LANGMUIR, D., Aqueous Environmental Chemistry, Prentice Hall, Upper Saddle River, NJ (1997).
- [212] PHILIPS, S., Hydrolysis and Formation Constants at 25°C, Lawrence Berkeley Lab. Rep. LBL-14313, Lawrence Berkeley Lab., CA (1982).
- [213] ALLARD, B., Actinide Solution Equilibria and Solubilities in Geologic Systems, SKB Rep. TR 83-35, SKB, Stockholm (1983).
- [214] JOHNSON, L., TAIT, J., Release of Segregated Nuclides From Spent Fuel, SKB Rep. 97-18, SKB, Stockholm (1997).
- [215] DACHEUX, N., et al., Investigation of the system  $\text{ThO}_2\text{-NpO}_2\text{-P}_2\text{O}_5$ : Solid solutions of thorium–neptunium (IV) phosphate–diphosphate, *J. Nucl. Mater.* **252** (1998) 179–186.
- [216] DACHEUX, N., et al., Actinides immobilization in new matrices based on solid solutions:  $\text{Th}_{4-x}\text{M}^{\text{IV}}_x(\text{PO}_4)_4\text{P}_2\text{O}_7$ , ( $\text{M}^{\text{IV}}=^{238}\text{U}$ ,  $^{239}\text{Pu}$ ), *J. Alloys and Compounds* **271–273** (1998) 236–239.
- [217] KOLB, W., WOJCIK, M., Enhanced radioactivity due to natural oil and gas production and related radiological problems, *Sci. Total Environ.* **45** (1985) 77–84.
- [218] PAIGE, C., et al., Solution equilibria for uranium ore processing: The  $\text{BaSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$  system, *Geochim. Cosmochim. Acta* **62** (1998) 15–23.
- [219] ZIELINSKI, R., OTTON, J., BUDAHN, J., Use of radium isotopes to determine the age and origin of radioactive barite at oil-field production sites, *Environ. Pollut.* **113** (2001) 299–309.
- [220] WOLERY, T., EQ3NR: A Computer Program for Geochemical Aqueous Speciation–Solubility Calculations, Rep. UCRL-MA-110662, Lawrence Livermore National Lab., CA (1992).
- [221] BERTETTI, F.P., PABALAN, R.T., ALMENDAREZ, M.G., “Studies of neptunium V sorption on quartz, clinoptilolite, montmorillonite, and  $\alpha$ -alumina”, Adsorption of Metals by Geomedia (JENNE, E., Ed.), Elsevier, Amsterdam (1998).
- [222] BIDOGLIO, G., OFFERMANN, P., SALTELLI, A., Neptunium migration in oxidizing clayey sand, *Appl. Geochem.* **2** (1987) 275–284.
- [223] STAMMOSE, D., et al., Sorption mechanisms of three actinides on a clayey mineral, *Applied Clay Sci.* **7** (1992) 225–238.
- [224] KUMATA, M., VANDERGRAAF, T., Experimental study on neptunium migration under in situ geochemical conditions, *J. Contam. Hydrol.* **35** (1998) 31–40.
- [225] McCUBBIN, D., LEONARD, K., Laboratory studies to investigate short-term oxidation and sorption behaviour of neptunium in artificial and natural seawater solutions, *Mar. Chem.* **56** (1997) 107–121.
- [226] DEGUELDRÉ, C., Retention of redox sensitive elements in aquifers — the case of neptunium, *Fuel and Energy Abs.* **37** (1996) 146.
- [227] NIITSU, Y., et al., Effects of humic acid on the sorption of neptunium(V) on kaolinite, *J. Nucl. Mater.* **248** (1997) 328–332.

- [228] RITTMANN, B.E., BANASZAK, J.E., REED, D.T., Reduction of Np(V) and precipitation of Np(IV) by an anaerobic microbial consortium, *Biodegradation* **13** 5 (2002) 329–342.
- [229] AARKOG, A., et al., Origin of technetium-99 and its use as a marine tracer, *Nature* **335** (1988) 338–340.
- [230] UNITED KINGDOM ENVIRONMENT AGENCY, Radioactive Substances Act 1993, Explanatory Document to Assist Public Consultation on Proposals for the Future Regulation of Technetium-99 Discharges from British Nuclear Fuels plc Sellafield into the Irish Sea, Environment Agency, London (2000).
- [231] DESMET, G., MYTTENAERE, C. (Eds), *Technetium in the Environment*, Elsevier, Amsterdam (1984).
- [232] BISHOP, G.P., BEETHAM, C.J., CUFF, Y.S., Review of Literature for Chlorine, Technetium, Iodine and Neptunium, Nirex Radioactive Waste Disposal Safety Studies Rep. NSS/R193, UK Nirex, Harwell, (1989).
- [233] BULMAN, R., COOPER, J. (Eds), *Speciation of Fission and Activation Products in the Environment*, Elsevier, Amsterdam (1985).
- [234] LEMIRE, R., GARISTO, F., The Solubility of U, Np, Pu, Th and Tc in a Geological Disposal Vault for Used Nuclear Fuel, Rep. 10009, Atomic Energy of Canada Limited, Mississauga, ON (1989).
- [235] PUIGDOMENECH, I., BRUNO, J., A Thermodynamic Database for Tc to Calculate Equilibrium Solubilities at Temperatures up to 300°C, SKB Rep. TR 95-09, SKB, Stockholm (1995).
- [236] RARD, J., A Critical Review of the Chemistry and Thermodynamics of Technetium and some of its Inorganic Compounds and Aqueous Species, Rep. UCRL-53440, Lawrence Livermore Lab., CA (1983).
- [237] RARD, J., et al., *Chemical Thermodynamics of Technetium*, Elsevier, Amsterdam (1999).
- [238] VANDERGRAAF, T., TICKNOR, K., GEORGE, I., Reactions between technetium in solution and iron-containing minerals under oxic and anoxic conditions, ACS Symp. Ser. **246** (1984) 25–43.
- [239] LIESER, K., BAUSCHER, C., Technetium in the hydrosphere and in the geosphere: I. Chemistry of technetium and iron in natural waters and influence of the redox potential on the sorption of technetium, *Radiochim. Acta* **42** (1987) 205–213.
- [240] CUI, D., ERIKSEN, T., Reduction of pertechnetate by ferrous iron in solution: Influence of sorbed and precipitated Fe(II), *Environ. Sci. Technol.* **30** (1996) 2259–2262.
- [241] AMAYA, T., KOBAYASHI, W., SUZUKI, K., Absorption study of the Tc(IV) on rocks and minerals under simulated geological conditions, *Mater. Res. Soc. Symp. Proc.* **353** (1995) 1005–1012.
- [242] LLOYD, J.R., MACASKIE, L.E., A novel phosphor imager based technique for monitoring the microbial reduction of technetium, *Appl. Environ. Microbiol.* **62** (1996) 578–582.

- [243] LLOYD, J.R., COLE, J.A., MACASKIE, L.E., Reduction and removal of heptavalent technetium from solution by *Escherichia coli*, J. Bacteriol. **179** (1997) 2014–2021.
- [244] LLOYD J.R., et al., Reduction of technetium by *Desulfovibrio desulfuricans*: Biocatalyst characterization and use in a flowthrough bioreactor, Appl. Environ. Microbiol. **65** (1999) 2691–2696.
- [245] SAWHNEY, B.L., Selective sorption and fixation of cations by clay minerals: A review, Clays Clay Miner. **20** (1972) 93–100.
- [246] CREMERS, A., et al., Quantitative analysis of radiocaesium retention in soils, Nature **335** (1988) 247–249.
- [247] COMANS, R.N.J., et al., Mobilization of radiocaesium in pore water of lake sediments, Nature **339** (1989) 367–369.
- [248] KONOPLEV, A.V., et al., Comparative study of  $^{137}\text{Cs}$  partitioning between solid and liquid phases in lakes Constance, Lugano and Vorse, J. Env. Radioact. **58** (2002) 1–11.
- [249] SWEECK, L., et al., “The specific interception potential of soils for radiocaesium”, Transfer of Radionuclides in Natural and Semi-natural Environments (DESMET, G., NASSIMBENI, P., BELLI, M., Eds), Elsevier Applied Science, Amsterdam (1990) 249–258.
- [250] KONOPLEV, A., KONOPLEVA, I., Parameterisation of  $^{137}\text{Cs}$  soil–plant transfer through key soil characteristics, Radiat. Biol. Radioecol. **39** 4 (1999) 455–461 (in Russian).
- [251] KONOPLEV, A.V., et al., Quantitative assessment of radiocaesium bioavailability in forest soils, Radiochim. Acta **88** (2000) 789–792.
- [252] BOSSEMEYER, D., SCHLOSSER, A., BAKKER, E., Specific cesium transport via the *Escherichia coli* Kup (TrkD)  $\text{K}^+$  uptake system, J. Bacteriol. **171** (1989) 2219–2221.
- [253] APPANNA, V.D., et al., A microbial model for caesium containment, Microbios **86** (1996) 121–126.
- [254] AVERY, S.V., CODD, G.A., GADD, G.M., Transport kinetics, cation inhibition and intracellular location of accumulated caesium in the green microalga *Chlorella salina*, J. Gen. Microbiol. **139** (1993) 827–834.
- [255] AVERY, S.V., CODD, G.A., GADD, G.M., Caesium transport in the cyanobacterium *Anabaena variabilis*: Kinetics and evidence for uptake via ammonium transport system(s), FEMS Microbiol. Lett. **95** (1992) 253–258.
- [256] DERKS, W.J.G., BORST-PAUWELS, G.W.F.H., Apparent three-site kinetics of  $\text{Cs}^+$  uptake by yeast, Physiol. Plant. **46** (1979) 241–246.
- [257] KONOPLEV, A.V., et al., Behaviour of long-lived Chernobyl radionuclides in a soil–water system, Analyst **117** (1992) 1041–1047.
- [258] SERNE, R.J., LEGORE, V.L.,  $^{90}\text{Sr}$  Adsorption–Desorption Properties and Sediment Characterization at 100 N-Area, Rep. PNL-10899, Pacific Northwest Laboratory, Richland, WA (1996).
- [259] BULGAKOV, A.A., KONOPLEV, A.V., Modeling long-term transformation of  $^{90}\text{Sr}$  speciation in soil, Russ. Soil Sci. (in press) (in Russian).

- [260] ANDERSON, S., APANNA, V.D., Microbial formation of crystalline strontium carbonate, *FEMS Microbiol. Lett.* **116** (1994) 42–48.
- [261] FERRIS, F.G., et al., Microbial precipitation of a strontium calcite phase at a groundwater discharge zone near Rock Creek, British Columbia, Canada, *Geomicrobiol. J.* **13** (1995) 57–67.
- [262] LLOYD, J.R., MACASKIE, L.E., “Bioremediation of radionuclide-containing wastewaters”, *Environmental microbe-metal interactions* (LOVLEY, D.R., Ed.), ASM Press, Washington, DC (2000) 277–327.
- [263] LANGMUIR, D., HERMAN, J.S., The mobility of thorium in natural waters at low temperatures, *Geochim. Cosmochim. Acta* **44** (1980) 1753–1766.
- [264] FELMY, A.R., RAI, D., MASON, M.J., The solubility of hydrous thorium(IV) oxide in chloride media: Development of an aqueous ion-interaction model, *Radiochim. Acta* **55** (1991) 177–185.
- [265] LANGMUIR, D., RIESE, A.C., The thermodynamic properties of radium, *Geochim. Cosmochim. Acta* **49** (1985) 1593–1601.
- [266] LANGMUIR, D., MELCHIOR, D., The geochemistry of Ca, Sr, Ba and Ra sulfates in some deep brines from the Palo Duro Basin, Texas, *Geochim. Cosmochim. Acta* **44** (1985) 1753–1766.
- [267] STURCHIO, N.C., et al., Radium geochemistry of ground waters in Paleozoic carbonate aquifers, mid-continent, USA, *Appl. Geochem.* **16** (2001) 109–122.
- [268] GNANAPRAGRASAM, E.K., LEWIS, B.-A., Elastic strain energy and the distribution coefficient of radium in solid solution with calcium salts, *Geochim. Cosmochim. Acta* **59** (1995) 5103–5111.
- [269] LANDA, E.R., Uranium mill tailings: Nuclear waste and natural laboratory for geochemical and radioecological investigations, *J. Environ. Radioact.* **77** (2004) 1–27.
- [270] BENES, P., BOROVEC, Z., STREJC, P., Interaction of radium with freshwater sediments and their mineral components: IV. Wastewater and riverbed sediments, *J. Radioanal. Nucl. Chem.* **99** (1986) 407–422.
- [271] BENES, P., BOROVEC, Z., STREJC, P., Interaction of radium with freshwater sediments and their mineral components: I. Ferric hydroxide and quartz, *J. Radioanal. Nucl. Chem.* **82** (1984) 275–285.
- [272] BENES, P., BOROVEC, Z., STREJC, P., Interaction of radium with freshwater sediments and their mineral components: II. Kaolinite and montmorillonite, *J. Radioanal. Nucl. Chem.* **89** (1985) 339–351.
- [273] BENES, P., BOROVEC, Z., STREJC, P., Interaction of radium with freshwater sediments and their mineral components: III. Muscovite and feldspar, *J. Radioanal. Nucl. Chem.* **98** (1986) 91–103.
- [274] BASSOT, L., et al., “Study of the radium sorption/desorption on goethite”, *International Radiation Protection Association (Proc. 10th Int. Conf. Hiroshima, 2000)*, IRPA, Paris (2000).
- [275] DE WINDT, L., PELLEGRINI, D., VAN DER LEE, J., Coupled modeling of cement/claystone interactions and radionuclide migration, *J. Contam. Hydrol.* **68** (2004) 165–182.

- [276] VOLESKY, B., *Biosorption of Heavy Metals*, CRC Press, Boca Raton, FL (1990).
- [277] DELAUNE, R., et al., *Mobility and Transport of Radium in Sediment and Waste Pits*, Final project report submitted to the Hazardous Substance Research Centre South and Southwest, Austin, TX (1996).
- [278] LANDA, E.R., MILLER, C.L., UPDEGRAAF, D.M., Release of  $^{226}\text{Ra}$  from uranium mill tailings by sulfate reducing bacteria, *Health Phys.* **51** (1986) 509–518.
- [279] LANDA, E.R., PHILLIPS, E.J.P., LOVLEY, D.R., Release of Ra from uranium mill tailings by microbial Fe(III) reduction, *Appl. Geochem.* **6** (1991) 647–652.
- [280] RICKARD, D.T., NRIAGU, J.O., “Aqueous environmental chemistry of lead”, *The Biogeochemistry of Lead in the Environment: Part A. Ecological Cycles* (NRIAGU, J.O., Ed.), Elsevier/North-Holland, New York (1978) 219–284.
- [281] MORIN, G., et al., Mineralogy of lead in soil developed on a Pb-mineralized sandstone (Ardèche, France), *Am. Mineral.* **86** (2001) 92–104.
- [282] GOLDSCHMIDT, V.M., *Geochemistry*, Oxford University Press, London (1954).
- [283] NRIAGU, J.O., MOORE, P.B. (Eds), *Phosphate Minerals*, Springer, New York (1984).
- [284] JOHNSON, C.E., PETRAS, R.J., Distribution of zinc and lead fractions within a forest spodosol, *Soil Sci. Soc. Am. J.* **62** (1998) 782–789.
- [285] O'REILLY, S.E., HOCELLA, M.F., Jr., Lead sorption efficiencies of natural and synthetic Mn and Fe-oxides, *Geochim. Cosmochim. Acta* **67** (2003) 4471–4487.
- [286] BITTEL, J.R., MILLER, R.J., Lead, cadmium, and calcium selectivity coefficients on montmorillonite, illite, and kaolinite, *J. Environ. Qual.* **3** (1974) 250–253.
- [287] STRAWN, D.G., SPARKS, D.L., The use of XAFS to distinguish between inner- and outer-sphere lead adsorption complexes on montmorillonite, *J. Colloid Interface Sci.* **216** (1999) 257–269.
- [288] PETERS, R.W., SHEM, L., Adsorption/desorption characteristics of lead on various types of soil, *Environ. Prog.* **11** (1992) 234–240.
- [289] RICHARDS, J.W., et al., Heavy metal resistance patterns of *Frankia* strains, *Appl. Environ. Microbiol.* **68** (2002) 923–927.
- [290] HARITHSA, S., KERKAR, S., LOKA BHARATHI, P.A., Mercury and lead tolerance in hypersaline sulfate-reducing bacteria, *Mar. Pollut. Bull.* **44** (2002) 726–732.
- [291] FEIN, J.B., et al., Bacterial effects on the mobilisation of cations from a weathered Pb-contaminated andesite, *Chem. Geol.* **158** (1999) 189–202.
- [292] SAYER, J.A., et al., Lead mineral transformation by fungi, *Curr. Biol.* **9** (1999) 691–694.
- [293] HUGHES, M.N., POOLE, R.K., *Metals and Microorganisms*, Chapman and Hall, New York (1989).
- [294] UNITED STATES DEPARTMENT OF ENERGY, *Uncertainty Management: Expediting Cleanup Through Contingency Planning*, Rep. DOE/EH/(CERCLA)-002, USDOE, Washington, DC (1997).

- [295] READ, D., FALCK, W.E. (Eds), CHEMVAL 2: A Co-ordinated Research Initiative for Evaluating and Enhancing Chemical Models in Radiological Risk Assessment, Rep. EUR 16648, Office for Official Publications of the European Communities, Luxembourg (1996).
- [296] VAN DER LEE, J., LOMENECH, C., Towards a common thermodynamic database for speciation models, *Radiochim. Acta* **92** (2004) 811–818.
- [297] CROSS, J., EWART, F., HATCHES — A Thermodynamic Database and Management System, Rep. NSS/R212, UK Nirex, Harwell (1990).
- [298] THOENEN, T., KULIK, D., Nagra/PSI Chemical Thermodynamic Database 01/01 for the GEM-Selektor (v.2-PSI) Geochemical Modelling Code: Release 28.02.03, Tech. Rep. TM-44-03-04, Paul Scherrer Institut, Würenlingen, Switzerland (2003).
- [299] YOSHIDA, Y., SASAMOTO, H., Establishment of Data Files of Thermodynamic Data Developed by OECD/NEA Part I: Thermodynamic Data of Np and Pu (2004), <http://migrationdb.jnc.go.jp/english.html>
- [300] JOHNSON, J.W., OELKERS, E.H., HELGESON, H.C., SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bar and 0 to 1000°C, *Comput. Geosci.* **18** (1992) 899–947.
- [301] HELGESON, H.C., et al., Summary and critique of the thermodynamic properties of rock-forming minerals, *Am. J. Sci. A* **278** (1978) 1–229.
- [302] SVERJENSKY, D.A., SHOCK, E.L., HELGESON, H.C., Prediction of the thermodynamic properties of aqueous metal complexes to 1000°C and 5 kb, *Geochim. Cosmochim. Acta* **61** (1997) 1359–1412.
- [303] SHOCK, E.L., et al., Inorganic species in geologic fluids: Correlations among standard molal thermodynamic properties of aqueous ions and hydroxide complexes, *Geochim. Cosmochim. Acta* **61** (1997) 907–950.
- [304] ROBIE, R.A., HEMINGWAY, B.S., Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar ( $10^5$  Pascals) pressure and at higher temperatures, *US Geol. Surv. Bull.* **2131** (1995) 461.
- [305] PARKHURST, D.L., APPELO, C.A.J., User's Guide to PHREEQC (Version 2): A Computer Program for Speciation, Batch-reaction, One-dimensional Transport, and Inverse Geochemical Calculations (1999), <http://www.interport.ne.jp/rist/htdocs/append/phreeqc2.7.txt>
- [306] PRICE, G.D., ROSS, N.L., *The Stability of Minerals*, Chapman Hall, London (1992).
- [307] OECD NUCLEAR ENERGY AGENCY, Survey of Thermodynamic and Kinetic Databases, Nuclear Science Committee, Rep. NEA/NSC/DOC(96)27, OECD, Paris (1996).
- [308] RICHTER, A., BRENDLER, V., BERNHARD, G., The mineral-specific thermodynamic sorption database RES<sup>3</sup>T: Concept description, implementation, and application towards contaminated systems, *Geochim. Cosmochim. Acta* **67** (2003) 397.

- [309] MADÉ, B., “Modélisation thermodynamique et cinétique des réactions géochimiques dans les interactions eau–roche”, Thesis, U.F.R. des Sciences de la Vie et de la Terre, Institut de Géologie, Université Louis Pasteur, Strasbourg (1991).
- [310] JACQUOT, E., “Modélisations thermodynamiques et cinétiques des réactions géochimiques dans les réservoirs profonds: application au site européen de recherche en géothermie profonde de Soultz-sous-Forêts (Bas-Rhin, France)”, Thesis, Université Louis Pasteur, Strasbourg (2000).
- [311] BULGAKOV, A.A., KONOPLEV, A.V., Diffusional model for radionuclide fixation in soils: A comparison with experimental data and other models, *Geochem. Int.* **39** (2001) 191–195.
- [312] KONOPLEV, A.V., BULGAKOV, A.A., “Kinetics of radionuclide leaching from fuel particles in the soil around the Chernobyl nuclear power plant”, Ten Years Terrestrial Radioecological Research Following the Chernobyl Accident (Proc. Int. Symp. Vienna, 1996), *Mitt. Österreichischen Bodenkundl. Ges.* **53** (1996) 61–67.
- [313] KONOPLEV, A.V., BULGAKOV, A.A., “Modelling the transformation processes of the Chernobyl origin  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  speciation in soils and bottom sediments”, Environmental Impact of Radioactive Releases (Proc. Int. Symp. Vienna, 1995), IAEA, Vienna (1995) 311–321.
- [314] KASHPAROV, V.A., et al., Kinetics of fuel particle weathering and  $^{90}\text{Sr}$  mobility in the Chernobyl 30 km exclusion zone, *Health Phys.* **76** (1999) 251–259.
- [315] KASHPAROV, V.A., et al., Dissolution kinetics of particles of irradiated Chernobyl nuclear fuel: Influence of pH and oxidation state on release of radionuclides in the contaminated soil of Chernobyl, *J. Nucl. Mater.* **279** (2000) 225–253.
- [316] BRENDLER, V., et al., Res<sup>3</sup>T-Rosendorf expert system for surface and sorption thermodynamics, *J. Contam. Hydrol.* **61** (2003) 281–291.
- [317] CHERY, L., SANJUAN, B., Recherche bibliographique sur les valeurs de  $K_d$  de 13 éléments dans 3 systèmes géologiques, Rep. ANDRA 620 RP BRG 92-035, 2 vols, ANDRA, Châtenay-Malabry, France (1992).
- [318] COUGHTREY, P.J., THORNE, M.C., Radionuclide Distribution and Transport in Terrestrial and Aquatic Ecosystems: A Critical Review of Data, A.A.Balkema, Rotterdam (1983).
- [319] SIBLEY, T.H., MYTTENAERE, C. (Eds), Application of Distribution Coefficients to Radiological Assessment Models, Elsevier Applied Science, Amsterdam (1986).
- [320] BENSON, L., A Tabulation and Evaluation of Ion Exchange Data on Smectites, Certain Zeolites and Basalt, Rep. 10541, Lawrence Berkeley Lab., CA (1980).
- [321] MAES, A., CREMERS, A., “Highly selective ion exchange in clay minerals and zeolites”, Geochemical Processes at Mineral Surfaces (DAVIS, J., HAYES, K., Eds), ACS Symp. Ser. **323** (1986) 254–295.
- [322] TAUGBOL, G., NEAL, C., Soil and stream water chemistry variations on acidic soils: Application of a cation exchange and mixing model at the catchment scale, *Sci. Total Environ.* **149** (1994) 83–95.



- [323] BRUGGENWERT, M.G.M., KAMPHORST, A., “Survey of experimental information on cation exchange in soil systems”, *Soil Chemistry: B. Physico-chemical Models* (BOLT, G.H., Ed.), *Developments in Soil Science* 58, Elsevier, Amsterdam (1979) 141–243.
- [324] BENSON, L.V., A tabulation and evaluation of ion exchange data on smectites, *Environ. Geol.* **4** (1982) 23–29.
- [325] MAES, A., CREMERS, A., “Highly selective ion exchange in clay minerals and zeolites”, *Geochemical Processes at Mineral Surfaces* (DAVIS, J.A., HAYES, K.F., Eds), *ACS Symp. Ser.* **323** (1986) 254–295.
- [326] DZOMBAK, D.A., MOREL, F.M.M., *Surface Complexation Modeling: Hydrous Ferric Oxide*, John Wiley, New York (1996).
- [327] BROWN, P.L., WANNER, H., *Predicted Formation Constants Using the Unified Theory of Metal Ion Complexation*, OECD, Paris (1987) 102 pp.
- [328] MORIYAMA, H., et al., *Chemical Analogy in the Case of Hydrolysis Species of F-Elements*, NEA Rep. 03168, OECD, Paris (2001) 145–156.
- [329] WOOD, B.J., “Crystal field electronic effects on the thermodynamic properties of  $\text{Fe}^{2+}$  minerals”, *Thermodynamics of Minerals and Melts: Advances in Physical Geochemistry* (NEWTON, R.C., NAVROTSKY, A., WOOD, B.J., Eds), Vol. 1, Springer, Berlin (1981) 63–84.
- [330] HEMINGWAY, B.S., HAAS, J.L., ROBINSON, G.R., Thermodynamical properties of selected minerals in the system  $\text{Al}_2\text{O}_3\text{-CaO-SiO}_2\text{-H}_2\text{O}$  at 298.15 K and 1 bar ( $10^5$  pascal) pressure and at higher temperatures, *US Geol. Surv. Bull.* **1544** (1982).
- [331] BERMAN, R.G., Internally consistent thermodynamic data for minerals in the system  $\text{Na}_2\text{O-K}_2\text{O-CaO-MgO-FeO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2\text{-TiO}_2\text{-H}_2\text{O-CO}_2$ , *J. Petrol.* **29** (1988) 445–522.
- [332] HOLLAND, T., POWELL, R., An internally consistent thermodynamic dataset for phases of petrological interest, *J. Metam. Geol.* **16** (1998) 309.
- [333] GOTTSCHALK, M., Internally consistent thermodynamic data for minerals in the system  $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-CaO-MgO-FeO-K}_2\text{O-Na}_2\text{O-H}_2\text{O-CO}_2$ , *Eur. J. Mineral.* **9** (1997) 175–223.
- [334] GARRELS, R., THOMPSON, M., A chemical model for seawater at 25°C and one atmosphere total pressure, *Am. J. Sci.* **260** (1962) 57–66.
- [335] ALLISON, J.D., BROWN, D.S., NOVO-GRADAC, K.J., MINTEQA2/PRODEFA2: A Geochemical Assessment Model for Environmental Systems, Version 3.0 User’s Manual, USEPA, Washington, DC (1991).
- [336] BETHKE, C.M., *The Geochemist’s Workbench®: A User’s Guide to Rxn, Act2, Tact, React, and Gplot*, Release 4.0 (2002), <http://www.geology.uiuc.edu/~bethke/>
- [337] KARPOV, I.K., CHUDNENKO, K.V., KULIK, D.A., Modeling chemical mass transfer in geochemical processes: Thermodynamic relations, conditions of equilibria, and numerical algorithms, *Am. J. Sci.* **297** (1997) 767–806.
- [338] VAN DER LEE, J., *Thermodynamic and Mathematical Concepts of CHESS*, Tech. Rep. LHM/RD/98/39, CIG-École des Mines de Paris, Fontainebleau (1998).



- [339] ANDRA, Référentiel Matériaux, Rep. C.RP.AMAT.01.060, ANDRA, Châtenay-Malabry, France (2001).
- [340] RUBIN, J., Transport of reacting solutes in porous media: Relation between mathematical nature of problem formulation and chemical nature of reactions, *Water Resour. Res.* **19** (1983) 1231–1252.
- [341] MANGOLD, D.C., TSANG, C.F., A summary of subsurface hydrological and hydrochemical models, *Rev. Geophys.* **29** 1 (1991) 51–71.
- [342] YEH, G.-T., TRIPATHI, V.S., A critical evaluation of recent developments in hydrogeochemical transport models of reactive multichemical components, *Water Resour. Res.* **25** (1989) 93–108.
- [343] ZYSSET, A., STAUFFER, F., DRACOS, T., Modelling of chemically reactive groundwater transport, *Water Resour. Res.* **30** (1994) 2217–2228.
- [344] READ, D., CHEMVAL Project, Report on Stages 3 and 4: Testing of Coupled Chemical Transport Models, Rep. EUR 13675EN, Office for Official Publications of the European Communities, Luxembourg (1991).
- [345] MILLER, C.W., BENSON, L.V., Simulation of solute transport in a chemically reactive heterogeneous system: Model development and application, *Water Resour. Res.* **19** (1983) 381–391.
- [346] LICHTNER, P.C., Continuum model for simultaneous chemical reactions and mass transport in hydrothermal systems, *Geochim. Cosmochim. Acta* **49** (1985) 779–800.
- [347] CARNAHAN, C.L., Simulation of uranium transport with variable temperature and oxidation potential: The computer program THCC, *Mater. Res. Soc. Symp. Proc.* **84** (1987) 713–721.
- [348] MOLZ, F.J., WIDDOWSON, M.A., BENEFIELD, L.D., Simulation of microbial dynamics coupled to nutrient and oxygen transport in porous media, *Water Resour. Res.* **22** (1986) 1207–1216.
- [349] MACQUARRIE, K.T.B., SUDICKY, E.A., FRIND, E.O., Simulation of biodegradable organic contaminants in groundwater: 1. Numerical formulation in principal directions, *Water Resour. Res.* **26** (1990) 207–222.
- [350] SAALTINK, M.W., CARRERA, J., AYORA, C., “On the numerical formulation of reactive transport problems”, *Computational Methods in Water Resources XI* (ALDAMA, A.A., et al., Eds), Computational Mechanics, Southampton (1996).
- [351] HUNTER, K.S., WANG, Y., VAN CAPPELLEN, P., Kinetic modeling of microbially-driven redox chemistry of subsurface environments: Coupling transport, microbial metabolism and geochemistry, *J. Hydrol.* **209** (1998) 53–80.
- [352] GRIFFIOEN, J., Comment on “Kinetic modeling of microbially-driven redox chemistry of subsurface environments: Coupling transport, microbial metabolism and geochemistry” by K.S. Hunter, Y. Wang and P. van Cappellen, *J. Hydrol.* **228** (2000) 285–288.
- [353] HUNTER, K.S., VAN CAPPELLEN, P., Reply to comment on “Kinetic modeling of microbially-driven redox chemistry of subsurface environments: Coupling transport, microbial metabolism and geochemistry” by J. Griffioen, *J. Hydrol.* **228** (2000) 289–291.

- [354] WANG, Y., PAPENGUTH, H.W., Kinetic modeling of microbially-driven redox chemistry of radionuclides in subsurface environments: Coupling transport, microbial metabolism and geochemistry, *J. Contam. Hydrol.* **47** (2001) 297–309.
- [355] ZYSSET, A., STAUFFER, F., DRACOS, T., “A kinetic biofilm concept for groundwater transport modelling”, *Transport and Reactive Processes in Aquifers* (Proc. Int. Symp. Zürich, 1994), A.A. Balkema, Rotterdam (1994) 451–456.
- [356] RIFAI, H.S., et al., “Simulation of natural attenuation with multiple electron acceptors”, *Intrinsic Bioremediation* (HINCHEE, R.E., WILSON, J.T., DOWNEY, D.C., Eds), Battelle Press, Columbus, OH (1995).
- [357] ZHENG, C., WANG, P., MT3DMS: A Modular Three-dimensional Multispecies Transport Model for Simulation of Advection, Dispersion, and Chemical Reactions of Contaminants in Groundwater Systems, Documentation and User's Guide, US Army Corps of Engineers, Contract Rep. SERDP-99-1, Engineer Research and Development Center, Washington, DC (1999).
- [358] MONOD, J., Growth of bacterial cultures, *Annu. Rev. Microbiol.* **3** (1949) 371–394.
- [359] SUDICKY, E.A., MACQUARRIE, K.T.B., “Behaviour of biodegradable organic contaminants in random stationary hydraulic conductivity fields”, *Contaminant Transport in Groundwater* (Proc. Int. Symp. Stuttgart, 1989) (KOBUS, H.E., KINZELBACH, W., Eds), A.A. Balkema, Rotterdam (1989) 307–315.
- [360] KINDRED, J.S., CELIA, M.A., Contaminant transport and biodegradation: 2. Conceptual model and test simulations, *Water Resour. Res.* **25** (1989) 1149–1159.
- [361] AZADPOUR-KEELEY, A., et al., Monitored natural attenuation of contaminants in the subsurface: Processes, *Ground Water Monit. Remed.* **21** 2 (2001) 97–107.
- [362] US ENVIRONMENTAL PROTECTION AGENCY, Guidance on Remedial Actions for Contaminated Groundwater at Superfund Sites, Office of Solid Waste and Emergency Response Directive 9283.1-2, USEPA, Washington, DC (1988) 110 pp.
- [363] DAVÉ, N.K., Panel Wetlands: A Case History of Partially Submerged Pyritic Uranium Tailings Under Water, MEND Project 3.12.2, Canada Centre for Mineral and Energy Technology, Ottawa, ON (1993).
- [364] SONGKASIRI, W., et al., “Bioremediation of neptunium(V) using lactate, hydrogen (H<sub>2</sub>), or Hydrogen Release Compound (HRC®)”, *Int. Symp. on In Situ and On-Site Bioremediation*, Orlando, 2003 (abstract).
- [365] SONGKASIRI, W., RITTMANN, B.E., REED, D.T., “Bio-reduction of neptunium(V) by *Shewanella* Alga with lactate or Hydrogen Release Compounds (HRC®) as an electron donor”, *Spectrum 2002* (Proc. Int. Conf. Reno, 2002), American Nuclear Society, La Grange Park, IL (2002).
- [366] CHATTERJEE, N.D., et al., The Bayesian approach to an internally consistent thermodynamic database: Theory, database, and generation of phase diagrams, *Contrib. Mineral. Petrol.* **133** (1998) 149–168.
- [367] COX, J.D., WAGMAN, D.D., MEDVEDEV, V.A., CODATA Key Values for Thermodynamics, Hemisphere Publishing, New York (1989).

- [368] SMITH, G.P., et al., Homepage of GRI-Mech™, Gas Research Institute, Des Plaines, IL (2004), [http://www.me.berkeley.edu/gri\\_mech/](http://www.me.berkeley.edu/gri_mech/)
- [369] BALL, J.W., NORDSTROM, D.K., User's Manual for WATEQ4F, with Revised Thermodynamic Database and Test Cases for Calculating Speciation of Major, Trace, and Redox Elements in Natural Waters, Open-File Rep. 91-183, US Geol. Surv., Reston, VA (1992) 189 pp.
- [370] NAUMOV, G.B., RYZHENKO, B.N., KHODAKOVSKY, I.L., Handbook of Thermodynamic Data — 1971, Atomizdat, Moscow (1971).
- [371] PHILLIPS, S.L., et al., Thermodynamic Tables for Nuclear Waste Isolation, an Aqueous Solutions Database, Vol. 1, Rep. LBL-22860, Lawrence Berkeley Laboratory, CA (1988) 181 pp.
- [372] WAGMAN, D.D., et al., The NBS tables of chemical thermodynamic properties, J. Phys. Chem. Ref. Data **11** Suppl. 2 (1982).

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**This report discusses the necessary pre-requisites, processes involved and applicability of monitored natural attenuation (MNA) as a non-intervention strategy for dealing with radioactive contamination. While MNA is de facto applied where residual contamination remains, it is emphasized that non-intervention does not equate to a ‘do nothing’ option. A thorough investigation of the site’s properties and the contaminant migration behaviour is needed for the safe application of the MNA concept. This report complements other recent publications dealing with low invasive remediation techniques and strategies.**