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Near-Field Solubility Constraints on Radionuclide Mobilization and their Influence on Waste Package Design [and Discussion]

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Near-field solubility constraints on radionuclide mobilization and their influence on waste package design

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The paper addresses the physical and chemical processes that can serve to immobilize waste radionuclides within the confines of an underground repository. These processes, which can be made largely independent of the chemical nature of the host rock, depend for their efficacy upon the maintenance of a very low flow rate of groundwater through the repository constituents.

The very long-lived waste products, in particular the actinides, are very insoluble in water under conditions of alkalinity and oxygen potential that will exist in a repository when cement is used as a backfill or as a matrix for the waste. The same chemical conditions tend to favour a fairly long life for steel containers. The paper suggests how these factors may be used to immobilize wastes and draws some conclusions on the relative value of the various engineered features of a repository.

Some natural geological analogues are explored as a means of assisting the extrapolation of waste behaviour over very long times.

1. INTRODUCTION

Long-lived radioactive wastes will generally require packaging for storage, transport and disposal purposes. It has been proposed (Flowers 1985) that, by careful attention to the specification of that packaging and of the other man-made components of a repository, the ‘near-field’ system can be very effective in its own right in controlling the return of waste radionuclides to man. This paper addresses the important features of that system and indicates some of the results that are being obtained from research into the physical and chemical processes concerned.

Table 1 lists a few of the important types of long-lived waste together with specific activity ranges, thermal powers and possible matrix materials. Wastes containing α-emitters at these levels remain very toxic for thousands of years, not unlike chemical wastes containing mercury, arsenic, cadmium or lead. The commonly advocated approach is that they be disposed of at depths of some hundreds of metres to eliminate risks from inadvertent intrusion or re-exposure by geological processes. The only credible risk then remains the contamination of aquifers or surface water by radionuclides leached out of the repository and transported in groundwater.

It is well known that by constructing a repository in rocks of low hydraulic conductivity, in a geological environment with low regional hydraulic gradients, the long potential migration pathways to man, coupled with the processes of sorption and diffusion of radionuclides in the rocks, can themselves provide sufficient delay and dispersion to reduce the ingestion risk from buried radioactive waste to very low levels (OECD 1984; KBS-3 1983). There are, however, advantages in designing the man-made parts of the waste disposal system so that they too

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TABLE 1. PROPERTIES OF SOME LONG-LIVED RADIOACTIVE WASTES (50 YEARS EX REACTOR)

	specific activity TBq m^{-3}†		approximate heat output	
waste material	α	$\beta\gamma$	W m^{-3}	matrix possibilities
high-level (PWR)	400	30000	2700	glass
fuel element hulls (AGR)	1	150	20	cement, polymer modified cement, polymer
Magnox sludges, resins and concentrates	0.3	50	5	
plutonium-contaminated material (Magnox)	1.5	2.5	0.5	

† 1 TBq = 10^{12} Bq = 27 Ci.

provide a guarantee against unacceptable levels of groundwater contamination. Such a policy can decouple the waste package specification from the requirement for prior knowledge of the detailed geological properties of the repository site and allows waste producers to package their waste in advance of the final selection of the site. It also provides a genuine redundancy of barriers to the return of the great majority of radionuclides to man, adding confidence to the overall safety case. It may be argued, with justification, that such obvious redundancy of safety measures is unnecessary in a technical sense (Burkholder 1983) but it could well be justified by the operational flexibility it allows and by the extra conviction which it gives to public presentation.

This paper takes as an example long-lived wastes emplaced in a cement-backfilled repository to demonstrate how estimates can be made of the maximum concentrations of radionuclides mobilized in the 'near-field'. That these 'contact' concentrations remain at very low levels, in many cases below accepted limits for drinking water, is a central feature of our case. For the purposes of the argument the wastes may be either of intermediate level, embedded in a cement matrix, or high-level vitrified wastes. It is a particular feature of our argument that the quantity of cement used as backfill in the repository is sufficiently large to dominate the natural groundwater chemistry over very long periods of time. In this respect the model differs considerably from models involving, for example, high-level waste in a clay backfill (KBS-3 1983).

The term 'near-field' is used in this paper to describe that part of a repository which is man made; it typically comprises three parts, sometimes called engineered barriers:

(i) the solid waste form, comprising radioactive waste embedded or dispersed in a solid matrix material;

(ii) the impermeable container, of known life, surrounding the waste form;

(iii) the cement backfill material, which conditions the chemistry of local groundwater and may also impede water flow around the container.

The 'far-field', which comprises the principal geological barriers, acts in series with the 'near-field' barriers; it is the subject of other papers in this symposium.

Expressed simply (Flowers 1983) the objective of near-field self-sufficiency would place the following requirements on the engineered barriers:

(*a*) the container would prevent any escape of waste radionuclides until the more soluble species, in particular ^{137}Cs, ^{90}Sr and ^{3}H, have decayed to levels where they will not cause significant contamination of the water in contact with the waste (500 years maximum);

(*b*) the waste-form matrix and backfill material would

(i) control the corrosion chemistry of the container as necessary to ensure its design life;

(ii) control, by chemical buffering and by provision of sorption surfaces, the effective solubility of the waste radionuclides remaining after the container is breached (actinides, ^{14}C, ^{129}I, ^{59}Ni and ^{99}Tc);

(iii) assist the natural geological environment in limiting water movement in the near-field.

2. The long-term behaviour of the 'near-field'

There are both natural and artificial influences at work in the performance of the near-field barriers and they are not independent of each other. For example the ambient groundwater chemistry is very strongly buffered by the cement backfill. The length of time over which this control of the important chemical parameters, such as pH, *Eh*, [CO_3^{2-}] and the concentration of other soluble ligands, will occur depends upon the rate of water movement through the backfill. That movement will be controlled by the host rock conditions but may be further reduced by the backfill itself. In addition to these influences the near-field may be affected by the radiolysis of water, and with high-level waste by a temperature transient of several hundred years.

2.1. *Behaviour of the waste form and the backfill*

The rate at which a radionuclide is mobilized from the waste form in contact with groundwater will be affected by near-field temperature, pH, *Eh* and water flow, and by the surface area and chemical stability of the waste form. It will also depend upon the chemical nature and the surface area of the backfill material placed in the repository with the waste.

Current experimental studies simulate the essentially zero-flow diffusion-dominated conditions expected in the near-field. The concentrations of individual radionuclides in solution are controlled not only by the breakdown of the waste form, but by solubility limits and the precipitation of phases that may be formed by reactions with the other near-field components. Savage (1984) has described this situation in detail for the case of vitrified waste in a granite host rock. Figure 1 shows the model dissolution behaviour of any solid waste form as a function

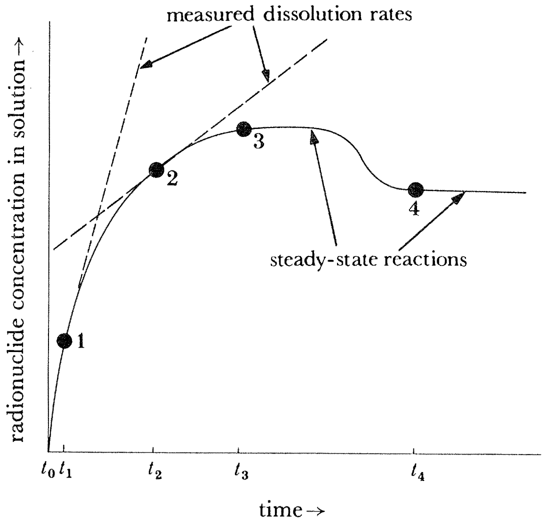

FIGURE 1. Waste-form dissolution behaviour as a function of time.

of time, and can effectively be taken to indicate the variable concentration levels at which a radionuclide can be found in near-field pore fluids. Until time t_3 (whose magnitude depends on temperature and surface area) a variety of 'leach rates' can be derived, generally decreasing with time. A leach rate extrapolated from this part of the curve gives no indication of any eventual solubility control and consequently will overestimate releases. At time t_3 the radionuclide will have entered solution at its saturation limit with respect to some particular solid phase (which may be the waste form, a sorbed layer or a newly precipitated mineral). After that we may expect a gradual decrease in solution concentration as further reactions occur to produce a thermodynamically more stable system (point 4 on figure 1). The initial steady-state solubility limit thus represents a conservative figure for radionuclide concentrations in solution at any time in the future. Because elevated temperatures decrease the time taken to develop well-crystallized secondary phases, they are thus not necessarily unfavourable to near-field repository performance, as is often assumed. It can be seen that the rate of release of an element from the waste after time t_3 is the product of its solubility and the pore-water movement.

The time taken to attain point 3 in figure 1 will vary depending on the waste form and backfill considered, as will the absolute solubility limit reached. Both cemented and vitrified wastes show a t_3 value of tens to hundreds of days over a wide temperature spectrum, whereas more durable materials such as supercalcine and SYNROC may be expected to take considerably longer to achieve steady state. It is thus possible that such waste forms will display kinetically controlled elemental release rates for quite long periods. It would, however, be wrong to judge waste forms on this factor alone. The solubility limit, taking into account the other materials in the near-field, must also be considered.

The equilibrium solubilities of specific elements from the waste form are thus very important parameters when one is considering not fast flowing water but the very slow diffusion and convection movements expected in a well sited underground repository. The roles of the container and of the solubility limits become clear when we divide the significant 'waste radionuclides' into two groups according to half-life.

In table 2 (Ewart *et al.* 1985*a*; Pryke 1985; Rees 1985 and personal communication) are listed the estimated solubilities, under alkaline reducing conditions, of all the radionuclides that could contribute significantly to the radioactivity of radioactive wastes; short-lived daughter products in equilibrium are not listed separately here. Those radionuclides of half-life less than 30 years (group A) can reasonably be kept out of contact with groundwater, by means of a suitable container, whereas movement of those of half-life greater than 30 years (group B) can be controlled by their inherent insolubility. Examination of group B reveals that there are three long-lived radionuclides (^{226}Ra, ^{14}C, ^{135}Cs) with appreciable solubilities, but transmission of these species to man is greatly inhibited by their low specific activities in wastes and, for ^{14}C, by isotopic dilution with stable isotopes. It should also be noted that whereas separated ^{129}I can, as suggested in the table, be immobilized as AgI, there will be small amounts of more soluble ^{129}I in some reprocessing wastes for which dilution and dispersion in the far-field is the only reliable control.

The particular groundwater condition of pH 11 and $Eh = -0.5$ V is used in this illustration because it corresponds to the chemical conditions in the pore water of a cement-grouted waste product in which oxygen potential is buffered by the $\mathrm{Fe^{II}/Fe^{III}}$ equilibrium. Reducing conditions of this order, which are important in maintaining Np and Tc in their insoluble forms, are ensured both by the host rock formation at depth and by the presence of steel containers.

Table 2. The half-lives and estimated solubilities of the significant waste radionuclides

radionuclide	half life/a	solubility† at 20 °C/M	solid phase	solution species
group A				
^{3}H‡	1.2×10^{1}	high	—	H_2O
^{60}Co‡	5.3	3×10^{-9}	$Co(OH)_2$	$HCoO_2^-$
^{90}Sr‡	2.9×10^{1}	10^{-4}	$SrCO_3$	Sr^{2+}
^{134}Cs	2.1	high	—	Cs^+
^{137}Cs‡	3.0×10^{1}			
^{244}Cm	1.8×10^{1}	10^{-10}	$Cm(OH)_3$	$Cm(OH)_3$
^{241}Pu	1.4×10^{1}	10^{-10}§	PuO_2 (hydrated)	$Pu(OH)_4$
group B				
^{238}Pu	8.8×10^{1}			
^{239}Pu	2.4×10^{4}			
^{240}Pu	6.6×10^{3}			
^{242}Pu	3.8×10^{5}			
^{241}Am	4.3×10^{2}	3×10^{-10}§	$Am(OH)_3$	$Am(OH)_2CO_3^-$
^{243}Am	7.4×10^{3}			
^{233}U	1.6×10^{5}	3×10^{-9}	UO_2 (hydrated)	$U(OH)_4$
^{234}U	2.4×10^{5}			
^{235}U	7.0×10^{8}			
^{236}U	2.3×10^{7}			
^{238}U	4.5×10^{9}			
^{237}Np	2.1×10^{6}	3×10^{-9}	NpO_2 (hydrated)	$Np(OH)_4$
^{229}Th	7.3×10^{3}	3×10^{-9}	ThO_2 (hydrated)	$Th(OH)_4$
^{230}Th	7.5×10^{4}			
^{232}Th	1.4×10^{10}			
^{231}Pa	3.3×10^{4}	probably low	—	
^{226}Ra	1.6×10^{3}	4×10^{-3}	$RaCO_3$	Ra^{2+}
^{14}C‡	5.7×10^{3}	10^{-5}	$CaCO_3$	CO_3^{2-}
^{59}Ni‡	7.5×10^{4}	6×10^{-8}	$Ni(OH)_2$	$HNiO_2^-$
^{63}Ni‡	1.0×10^{2}			
^{79}Se‡	6.5×10^{4}	5×10^{-12}	Se	HSe^-
^{93}Zr‡	1.5×10^{6}	10^{-7}	ZrO_2 (hydrated)	$HZrO_3^-$
^{99}Tc	2.1×10^{5}	10^{-8}	$TcO(OH)_2$	$TcO(OH)_2$
^{126}Sn‡	1.0×10^{5}	7×10^{-10}	SnO_2	SnO_3^{2-}
^{129}I	1.6×10^{7}	10^{-8}	AgI	I^-
^{135}Cs‡	2.0×10^{6}	high	—	Cs^+
^{151}Sm	9.0×10^{1}	10^{-10}	$Sm(OH)_3$	$Sm(OH)_3$

† Element solubility in water at pH 11, $Eh = -0.5$ V, $[CO_3^{2-}] = 10^{-5}$ M, equivalent to aged cement in which oxygen potential is buffered by Fe^{2+}/Fe^{3+}; no adsorption on solid surfaces assumed.

‡ The effective solubility of these radionuclides would be further reduced through isotopic dilution by natural isotopes and/or stable fission products also present in the waste package.

§ Data from experimental results of Ewart *et al.* (1986*a*).

A further important feature of the near-field, not represented in table 2, that will affect the concentrations of the group B radionuclides in solution is the extensive surface area provided by the cement components in the grout and backfill and by any clay minerals that may also be used as backfill. It is probable that adsorption of species such as $Pu(OH)_4$, $Am(OH)_3$ and $HNiO_2^-$ on these surfaces will reduce their equilibrium solubilities far below those shown in table 2. Some preliminary measurements (Greenfield *et al.* 1984) have been made in cement grouted intermediate level wastes and the results (table 3) do indicate that trend. In these experiments, conducted at pH 12.7 but at atmospheric oxygen potential, the measured solubilities of Pu, Am and Np contained in a Magnox swarf-cement waste form correspond to a level of water

Table 3. Empirical data on solubility of actinides from cement-grouted Magnox cladding waste at 20 °C (oxidizing conditions)

radionuclide	solubility/M
^{237}Np	2.1×10^{-10}
^{241}Am	5×10^{-12}
^{239}Pu/^{240}Pu	1.3×10^{-10}

contamination that, on the absurd assumption that it could compose a sole source of drinking water for an individual, would result in an annual committed effective dose equivalent of only about 100 mSv. Very similar results have recently been reported by Ewart *et al.* (1985*b*) and these workers also have in progress some equilibrations in which oxygen potential is carefully controlled within the reducing régime relevant to repository conditions. In effect, the adsorbed state of the solution species, rather than the solid oxide phase itself, may be the most stable state when these dilute waste mixtures are equilibrated with water. More experimental work is required on this effect, but it seems certain that actual near-field concentrations will be well below the estimates of elemental solubility given in table 2.

2.2. *Model of near-field performance of a cement-based waste*

The effect (Chapman *et al.* 1981; Atkinson 1984; Hughes *et al.* 1983) of these low solution concentrations upon the rate of movement of radionuclides from the near-field of an underground repository may be estimated by considering the behaviour of an intermediate-level waste form (AGR fuel element hulls embedded in a cement matrix) emplaced in a cement backfilled repository, after the general failure by corrosion of the containers in which the waste form was originally sealed. It is assumed that the repository is a 40 m cube of cement, embedded in a host rock formation of similar hydraulic conductivity, whose value is varied to allow, in a simple fashion, consideration of different groundwater flow rates. The waste form is assumed to occupy 50% of the repository volume as spheres of 0.1 m radius in which specific radionuclides are initially present at concentration C_0. The intrinsic diffusion coefficient for water in the cement and the host rock is assumed to be 10^{-11} m^2 s^{-1}. Using the following typical values of variables specific to two elements chosen to illustrate the model, i.e.:

	Cs	Pu
equilibrium aqueous concentration	10^{-3}	10^{-10} M;
C_0, initial concentration in waste form	9×10^{-4}	3×10^{-4} M;
leach rate of waste form under fast water flow conditions (Ross *et al.* 1983; Atkinson *et al.* 1985)	10^{-2}	10^{-9} m a^{-1};

we can calculate the rates at which Cs and Pu would leave the repository in groundwater as a function of the water flow-rate per unit area of repository section (F). The results are shown in figure 2.

The effect of varying water flow-rate is to reveal three régimes. With F below about 10^{-11} m s^{-1} diffusion of water through the pore space of the repository materials is the dominant mechanism; it results in a greater fractional release rate for Cs than for Pu because a much greater fraction of Cs is in the aqueous phase at equilibrium. With F between 10^{-11} and 10^{-7} m s^{-1} the water leaving the repository is saturated with the waste radionuclides under near-field chemical conditions so that fractional release rate is proportional to water flow. At

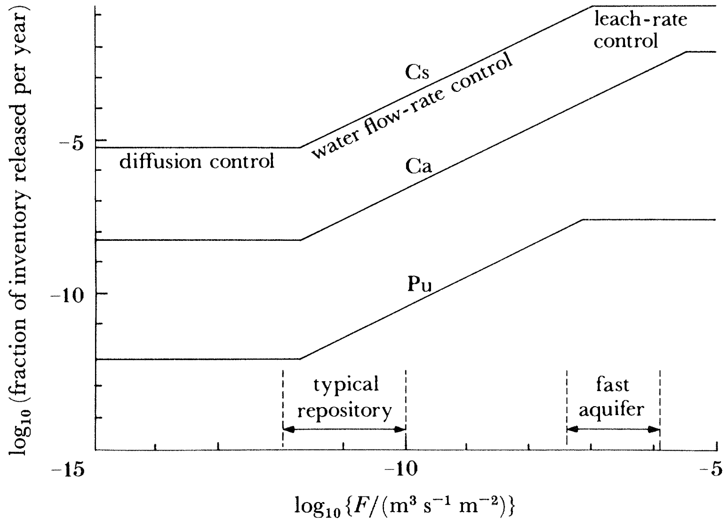

FIGURE 2. Rate of release of Cs, Ca and Pu from a cement-based repository.

higher F values, release rate is controlled by kinetic factors in the removal of material from the surface of the waste form. However, such high F values are associated with aquifers which are inherently unsuitable for a repository.

On figure 2 a probable range of water flow rates in an underground repository host rock would be in the range 10^{-12} to 10^{-10} $m^3\ s^{-1}$ per square metre of repository section. At such low flows the fractional release rates per year of a very soluble (Cs) and a very insoluble (Pu) species are approximately 10^{-4} and 10^{-11} respectively, illustrating the importance of intrinsic solubility and groundwater flow rate, rather than the kinetics of leaching, in confining waste radionuclides within the repository until they have decayed. Also shown in figure 2 is the fractional release rate of the calcium silicate cement matrix itself (Roy *et al.* 1982). Because this is greater than that for plutonium it appears that, in reality, plutonium confinement within the near-field will, in the very long term (beyond 1 Ma), be determined by mineralization processes after the cement has gone. It is important to note that control of group B radionuclide release by this mechanism does not make assumptions about the physical integrity of the container, the waste matrix or any other near-field material; the control depends upon choice of a geological environment and a host rock with low water flow and upon the intrinsic chemical properties of the materials placed in the repository.

It is relevant to consider how long the required conditions are likely to be chemically buffered by the repository contents. This depends particularly upon the time taken for flowing groundwater to dissolve out calcium and iron. As an illustration of how pH would change with time in a cement backfill, figure 3 shows (Atkinson & Hearne 1984; Atkinson 1985) how the average pH of water in equilibrium with cement in the repository would change as water passes through it, assuming that our model repository contains 185 kg of Portland cement per cubic metre. After an initial short period during which alkali hydroxides are removed there is a long period of buffering by the $Ca(OH)_2$ phase. A further slow decrease in pH follows as calcium is leached out of the calcium silicate gel and finally the pH falls to 8.3 in equilibrium with the residual calcium carbonate. Even assuming a water flow rate of 10^{-10} $m^3\ s^{-1}$ per unit area of the repository the average pH of near-field groundwater might be expected to remain above

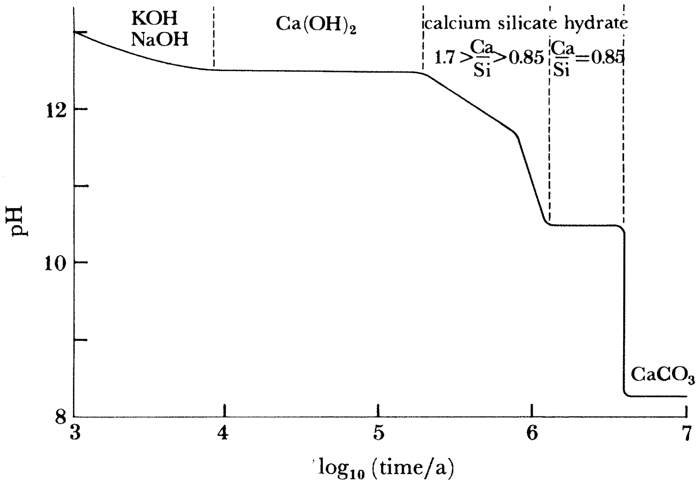

FIGURE 3. Evolution of average pH with time for a cement-based repository, based on the assumptions that the water flow rate is 10^{-10} m^3 s^{-1} per square metre section of repository, and that the average cement content is 185 kg m^{-3}.

10.5 for more than 1 Ma. Consideration of the pH profile across the repository shows that under diffusion dominated conditions a calcium depleted region of about 1 m thickness would develop over a 1 Ma period; this would not impinge upon the embedded waste form. At higher flow rates the use of the average pH change is conservative because eluted radionuclides would be carried forward into the region of higher Ca content.

2.3. *The container*

The waste container will ensure that groundwater does not reach the waste until the more soluble group A radionuclides have substantially decayed. After that, the container has no essential role as a physical barrier. The discussion below is therefore concerned only with its performance over that relatively short time, which will depend upon the radionuclide content of the particular waste but will not normally exceed about 500 years.

A container may be designed to provide a corrosion thickness allowance or to be corrosion resistant. Carbon steel has been evaluated in the U.K. as an example of the former; titanium alloys and stainless steels are under investigation in the latter context (Marsh *et al.* 1983).

The rate of general corrosion of carbon steel under the alkaline and reducing conditions of a cement-grouted deep repository would be limited by the rate of the cathode reactions,

oxygen reduction, $$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-,$$

or the much slower water reduction reaction,

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2,$$

and therefore the rate of introduction of oxygen from the surrounding groundwater is very important. If the pH is maintained above 10 by the buffering action of cement, and oxygen transport is limited by diffusion in the cement, then the general corrosion rate would be limited to a few micrometres per year at 25 °C. In practice, allowance would also be made for possible pitting corrosion due to chloride and sulphate ions so that a 300 year lifetime container might be specified to have a wall thickness of around 30 mm. Internal corrosion, either of a general or localized form, sustained by radiolytic oxygen would also be accommodated within that corrosion allowance.

A container made from corrosion-resistant titanium or stainless steel depends entirely upon the stability of the passivating oxide film for its long life under disposal conditions. The research done on conditions for stability of the TiO_2 film on titanium indicates that it would be maintained even under quite reducing conditions at pH values above 7 (Naish & Marsh 1983). The difficulty, however, is in proving that stresses and crevices will not lead to local film breakdown over very long times.

Concrete is itself a possible container material (Atkinson & Hearne 1984). With a diffusion coefficient of less than 10^{-12} m^2 s^{-1} for aqueous solutes, and a hydraulic conductivity of around 10^{-12} m s^{-1}, an effective 300 year container can be made with a few centimetres thickness of cement. The main question here concerns the durability of the material under conditions of calcium leaching and sulphate attack. It is estimated that a 1 m thick reinforced concrete section made of sulphate-resistant Portland cement has a structural life of at least 500 years; current research is exploring the associated changes in diffusivity and permeability.

Radiolysis of water and of organic material liberates hydrogen; typically a 0.5 m^3 drum of cemented waste might yield 1 m^3 of hydrogen over a 100 year period. In some cases there may also be a slow evolution of hydrogen from chemical reaction between metals and water. Waste drums might therefore be vented but the small apertures required would not compromise the radionuclide containment function under disposal conditions.

2.4. *Other influences on the behaviour of the near-field*

There are two further influences upon repository chemistry that may be important under particular circumstances and which are the subject of current research. Radiation damage, particularly from the α-particle dose to waste forms, can cause structural changes that are of interest during storage of waste drums. More important to disposal, however, is the radiolysis of water in the cement grout because this could result in a rise in oxygen potential if the hydrogen product escaped preferentially from the system. Present indications (Vejmelka & Sambell 1984) are that the oxygen accumulation within that part of the cement most exposed to radiation would not exceed a few tenths of a milliequivalent per gram of solid, having absorbed a dose of 10^7 Gy; this would allow effective buffering of *Eh* by the presence of Fe^{II}. Since the fate of hydrogen in the near-field is uncertain, and some recombination may occur, this example represents a worst case.

The second area is the effect of organic materials such as cellulose, solvents and plastics on container life and on the solubility of long-lived waste radionuclides. The production of soluble ligands, either by radiolysis or microbiological degradation (Rushbrook 1985) of these materials could in principle increase the solubility of, for example, plutonium in the near-field groundwater. Corrosive metabolic products of microbial growth might influence container corrosion rates.

The role of microorganisms in near-field geochemistry has come under increased study. Several reviews (West *et al.* 1982, 1985) demonstrate the ability of microbes to be introduced into and survive in the adverse conditions of a waste repository, and more specific studies (Mayfield & Barker 1982) have confirmed the potential for introducing microorganisms in a clay backfill.

Introduced populations may flourish briefly after closure, depending on the availability of nutrients *in situ* or transported in by groundwaters, and this period may be sufficient to enhance local corrosion of materials. Particular attention needs to be paid to the potential corrosion of steel and degradation of cement used as container materials. Repository systems making extensive use of cements will have a very high pH environment and so the significance of alkalophilic or alkali-tolerant species needs to be established. In general there would appear to be considerably less likelihood of adverse biological activity in this type of environment than in a repository backfilled with clays from surface outcrop. Extensive background data on potential contaminants have been collected and current studies are endeavouring to model system energetics and biodegradation effects more precisely to determine whether any prophylactic measures would need to be taken to minimize contamination during waste-form production or disposal operations.

3. Geological evidence for long-term near-field processes

The scheme described above relies on the maintenance of low groundwater fluxes in the near-field. Confidence in such predictions over timescales of 10^3–10^6 years can only reasonably be obtained by studying analogous factors or processes in the natural environment, owing to the difficulties inherent in extrapolating experimental data by more than one or two orders of magnitude of time. Natural analogues are increasingly being used for model validation, but must be tightly constrained to specific chemical processes (Chapman *et al.* 1984).

Geological evidence for extremely low advection rates in clay formations can be derived from analyses of pore waters in clays and intervening aquifer formations. Increasing solute concentrations generally indicate an approach to original saline formation water compositions in marine sediments, or long episodes of equilibration during diagenesis. This evidence, along with information on stable isotope and natural series radioisotope contents, can be used to infer residence times of water within particular formations, or potential dilution by deeply penetrating fresh surface waters that may recharge the system. A good example of this approach is a recent study of groundwater behaviour in the Oxford and Gault-Kimmeridge clays and the intervening Corallian aquifer in the south Oxfordshire area (Alexander & Brightman 1986; Black *et al.* 1985). By a combination of direct observation of hydraulic properties of the formations and geochemical data on the groundwaters (for example U/Th activity ratios, radiogenic ^{4}He content, salinities, and ^{14}C values, from which apparent 'ages' and consequently degrees of mixing could be inferred) it was possible to model potential groundwater transit times through the clays, both downwards and upwards into the aquifer. Typical values are in the order of 10^5–10^6 years, with subsequent transit times to the 'biosphere' within the aquifer of the same order of magnitude. These values represent only the rate of water movement. Dissolved cations would be subject to additional chemical retardation processes. It must be borne in mind that such sluggish groundwater conditions are as dependent on the regional hydrogeological environment as they are on local rock properties. Consequently adequate regional studies are essential in site assessment.

Similar data can be obtained from groundwaters in deep crystalline rocks, where essentially stagnant saline waters have been encountered, with only limited mixing with fresh surface waters (Fritz & Frape 1982). Fractured rocks are, however, less predictable on a regional scale than clay–mixed-sediment sequences because major water-bearing fractures can occur in otherwise tight rock. Thus even though bulk hydraulic conductivities in such formations may be much less than 10^{-9} m s^{-1} at depth, the potential exists for relatively rapid transit routes. Although such zones may be avoidable, the backfill does consequently take on more importance in fractured rocks, where detectable flow may occur locally.

Eisenbud *et al.* (1984) have demonstrated the effect of solubility limitation on the large-scale, long-term mobilization of radionuclides from a thorium deposit at Morro do Ferro in Brazil. Thorium is considered to be a good analogue for the behaviour of $\mathrm{Pu^{IV}}$. Despite strong weathering processes in a dominantly oxidizing near-surface groundwater system, Th concentrations in effluent stream waters average 0.05 μg l^{-2} (2×10^{-10} M). This is very similar to the preliminary values obtained (table 3) for Pu solubility under conditions where extensive surfaces are present for sorption. The Morro do Ferro site has experienced highly adverse conditions of surface weathering and rapid groundwater flow, so this, like other natural analogues, lends strong support to the concepts outlined earlier.

4. Conclusions

The near-field and far-field barrier systems act together to control releases of radionuclides from a waste repository. The assurance of limited near-field groundwater flow provided by the host rock formation does, however, permit the decoupling of the numerical performance of the two halves of the system. This allows the specifications for the waste form, container and backfill to be decided in advance of a detailed knowledge of the geological properties of an eventual site, thus allowing useful operational flexibility in the early stages of waste management.

A useful basis for near-field specification is the provision of a container of limited lifetime (up to about 500 years) that contains the more soluble short-lived radionuclides (here termed group A) until they have decayed, combined with a waste form and backfill that buffer the near-field pore-water chemistry so as to ensure that long-lived (group B) radionuclide solubilities are extremely low. The specification of container life in particular will depend upon the concentrations of group A radionuclides in the waste.

The example used in this paper is a long-lived intermediate-level waste in a cement matrix embedded in a cement backfill. Equilibrium concentrations in the near-field, for group B radionuclides, are likely to be within a factor of 100 of drinking water limits based upon the ICRP limit for radiation dose to members of the public.

This approach can be applied generally to all waste types. For high-level wastes it is necessary to take into account the higher temperature and radiation dose rate when estimating or measuring container corrosion rates and radionuclide solubilities. For actinide-contaminated wastes from which group A radionuclides are absent, the container has no essential role after disposal.

The natural geological environment provides evidence for the long-term nature of many of the near-field processes important to repository performance. In particular, natural analogues for the solubility limitation of actinide mobilization from uranium and thorium deposits by groundwater, and for the long-term preservation of low-flow régimes, lend support to the model described here. Additional studies are clearly required in this area, as are further data on the possible effects of biodegradation and radiolysis of organic materials on container corrosion and on equilibrium solubilities of long-lived radionuclides.

The separation of near-field and far-field specifications is a very useful procedure in the operational task of managing radioactive wastes, offering practical and presentational advantages. However, for regulatory purposes and for assessment of environmental impact of a repository it will be essential to perform an assessment of the performance of the complete system comprising near-field, far-field and biosphere.

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Discussion

J. E. Antill (*Central Electricity Generating Board, Berkeley Nuclear Laboratories, Gloucestershire, U.K.*). The authors have covered comprehensively the transport of species in solution. Another common transport mechanism involving particles, and colloids could be important in the present context. Have the authors arguments to discount such a mechanism?

R. H. Flowers. This is a question which is not yet resolved and on which research is still necessary. However, there are indications that colloidal and larger particles will be effectively filtered out by passage through the far-field and, in fact, the solubility measurements made under near-field conditions do not reveal a significant colloidal fraction.

S. H. U. Bowie, F.R.S. (*Tanyard Farm, Clapton, Crewkerne, Somerset, U.K.*). This concept depends very much on the amount and composition of groundwater and is therefore site-dependent. To what extent have time-dependent geological events been taken into account in, for example, ensuring that the chemistry of the repository does not change over a period of 10000 years?

R. H. Flowers. It is a particular feature of our proposal that local groundwater composition will be unimportant, owing to the buffering of pH by the cement present in the near-field. However, it will still be necessary to predict the probability and consequence of improbable events, such as a major increase in groundwater flow. In that case, the chemistry of the local water could be relevant.