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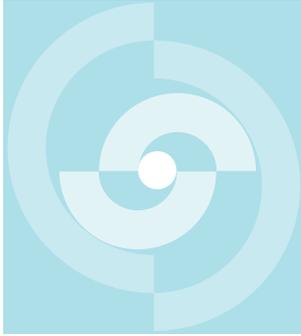
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# **TECHNICAL REPORT 88-26**

## **THE NEAR-FIELD GEOCHEMISTRY OF HLW DISPOSAL IN AN ARGILLACEOUS HOST ROCK**

Ian. G. McKinley

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## SUMMARY

Current concepts in Switzerland envisage the disposal of vitrified high-level waste (HLW), encapsulated in massive steel canisters, horizontally into tunnels which are backfilled with compacted bentonite. In the Project Gewähr 1985 study, the geochemical aspects of the performance of these barriers in a repository situated at a depth of  $\approx 1300$  m in a crystalline host-rock were evaluated. This report extends that analysis to consider an alternative repository concept at a depth of  $\approx 850$  m in an argillaceous host rock.

In general, the longevity of the engineered barriers is little affected by the choice of host rock - the analysis predicts that bentonite will retain its favourable physical and chemical properties for more than  $10^6$  years, the canister will last more than  $10^3$  years and the complete degradation of the glass matrix will take over  $10^5$  years. These components also ensure that most of the near-field is chemically buffered in reducing, mildly alkaline conditions. After failure of the mechanical integrity of the canister, the release of many important nuclides is further constrained by their low solubilities. Transport of dissolved radionuclides occurs in the bentonite only by diffusion, which is limited by various retardation mechanisms (sorption, anion exclusion, etc.). One of the key rôles of the bentonite in this regard is to act as a filter, preventing migration of particulate or colloidal species.

Various factors are, however, specific to the argillaceous host rock case. Rock mechanical constraints necessitate the use of a liner during the operational phase and this liner may be impractical to remove. Because oxidation of the host rock is of potential concern, it is desirable that this liner be as tight as possible but, after waste emplacement, there are advantages to it being homogeneously permeable. The geochemistry of the engineered barrier/rock interface is generally more complex in the sediment case relative to crystalline - due not only to potential oxidation but also to the possible increased significance of natural organics, colloids and microbial activity.

In conclusion, the expected radionuclide release rates from the near-field are very low, even with fairly conservative assumptions on the performance of various barriers. There are indications that a more realistic analysis would demonstrate negligible releases of almost all key nuclides. The justification of such a treatment depends, however, on building up a more fundamental understanding of some of the processes involved and validation of the models/databases used by a variety of methods, possibly including natural analogue studies.

## ZUSAMMENFASSUNG

Die gegenwärtigen Konzepte in der Schweiz sehen vor, verglaste, radioaktive Abfälle (HAA) - in massiven Stahlbehältern verkapselt - horizontal in Tunneln, die mit verdichtetem Bentonit verfüllt werden, zu entsorgen. In der Studie "Projekt Gewähr 1985" wurden die geochemischen Aspekte der Wirkung dieser Sicherheitsbarrieren für ein Endlager in rund 1300 m Tiefe im kristallinen Wirtgestein studiert. Dieser Bericht setzt die Analyse fort, um ein alternatives Endlagerkonzept in einer Tiefe von rund 850 m in einem tonigen Gestein zu berücksichtigen.

Im allgemeinen wird die Langlebigkeit der technischen Barrieren nur wenig durch die Wahl des Wirtgesteins beeinflusst - die Analyse prognostiziert, dass Bentonit seine günstigen physikalischen und chemischen Eigenschaften länger als  $10^6$  Jahre beibehalten wird, dass der Stahlbehälter länger als  $10^3$  Jahre halten wird und der totale Zerfall der Glasmatrix mehr als  $10^5$  Jahre dauern wird. Diese Komponenten sorgen auch dafür, dass der Grossteil des Nahfeldes unter reduzierenden, leicht alkalischen Bedingungen chemisch gepuffert wird. Bei Versagen der mechanischen Integrität des Behälters wird die Freisetzung vieler wichtiger Nuklide durch ihre niedrigen Löslichkeiten eingeschränkt. Im Bentonit findet der Transport gelöster Nuklide nur durch Diffusion statt, welche zudem noch durch verschiedene Verzögerungsmechanismen (Sorption, Anionausschluss, usw.) weiter eingeschränkt wird. Eine der diesbezüglichen Schlüsselrollen des Bentonits ist es, sich als Filter zu verhalten, um die Migration von Partikeln oder kolloidaler Spezies zu verhindern.

Im Falle eines tonigen Wirtgesteins treten jedoch mehrere spezifische Faktoren auf. Felsmechanische Gegebenheiten zwingen zur Benützung einer Auskleidung während der Betriebsphase, zudem kann sich die Entfernung dieser Auskleidung als unpraktisch erweisen. Da die Oxidation des Wirtgesteins von potentieller Wichtigkeit ist, ist es wünschenswert, diese Auskleidung so dicht wie möglich zu gestalten; nach der Abfalleinlagerung wäre es jedoch von Vorteil, wenn sie homogen durchlässig wäre. Die Geochemie des Gesteins/Barrieren-Kontaktes ist im allgemeinen komplexer in Sedimentgesteinen als im Kristallin, was nicht nur auf die potentielle Oxidation, sondern auch auf die möglicherweise steigende Bedeutung natürlicher, organischer Stoffe, Kolloide und auf mikrobielle Aktivität zurückzuführen ist.

Zum Schluss kann gesagt werden, dass die erwarteten Radionuklid-Freisetzungsraten aus dem Nahfeld sehr gering sind, sogar mit ziemlich konservativen Annahmen für das Verhalten verschiedener Barrieren. Es gibt Hinweise dafür, dass eine realistischere Analyse für beinahe alle wichtigen Nuklide vernachlässigbare Freisetzungen nachweisen würde. Die Rechtfertigung einer solchen Analyse hängt jedoch vom Erreichen eines tieferen Verständnisses einiger involvierter Prozesse und von einer Validierung der gebrauchten Modelle/Datenbasen ab, möglicherweise unter Einbeziehung von Naturanaloga.

## RESUME

Actuellement en Suisse, on envisage d'éliminer les déchets vitrifiés de haute activité (DHA) - encapsulés dans des conteneurs en acier massif - à l'intérieur de tunnels remplis de bentonite compactée. On a évalué, dans l'étude du projet Garantie 1985, la performance géochimique de ces barrières pour un dépôt final situé à 1300 mètres de profondeur à l'intérieur de la roche d'accueil cristalline. L'analyse considère ensuite une autre conception de stockage final, cette fois-ci à 850 mètres de profondeur à l'intérieur d'une roche argileuse.

En général, le choix de la roche d'accueil influence peu la longévité des barrières ouvragées - selon l'analyse, la bentonite gardera des propriétés physiques et chimiques favorables plus de  $10^6$  ans, le conteneur en acier durera plus de  $10^3$  ans et il faudra plus de  $10^5$  ans avant que la matrice de verre ne se dégrade totalement. Ces composantes veillent donc à ce que la majeure partie du champ proche soit chimiquement tamponnée dans des conditions réductrices, légèrement alcalines. En cas de défaillance de l'intégrité du conteneur, le relâchement de nombreux nucléïdes importants sera contenu encore par ses solubilités basses. Dans la bentonite, le transport de nucléïdes dissous n'a lieu que par diffusion, cette dernière étant également limitée par différents mécanismes de retardement (sorption, exclusion d'anions, etc.). Ici, un des rôles clés de la bentonite consiste à agir comme un filtre qui empêche la migration d'espèces colloïdales ou en particules.

Plusieurs facteurs sont toutefois spécifiques à la roche d'accueil argileuse. Du fait de contraintes géomécaniques, il est nécessaire d'utiliser, au cours de la phase d'exploitation, un revêtement que s'avère parfois peu pratique à enlever. Vu que l'oxydation de la roche d'accueil peut être importante, il est souhaitable d'avoir un revêtement aussi étanche que possible; après l'emmagasinage des déchets, il serait pourtant opportun qu'il soit perméable de façon homogène. La géochimie du contact roche/barrière est en général plus complexe dans les roches sédimentaires que dans le cristallin; cela est dû non seulement à l'oxydation potentielle, mais aussi à l'importance potentiellement croissante de substances organiques naturelles et de colloïdes, ainsi qu'à l'activité microbienne.

En conséquence, on peut dire que le relâchement escompté des radionucléïdes hors du champ proche est très faible, même si l'on part d'hypothèses assez prudentes à propos du comportement des différentes barrières. Une analyse plus réaliste démontrerait sans doute un relâchement négligeable de presque tous les radionucléïdes les plus importants. Une telle analyse ne peut toutefois se justifier que si l'on comprend quelques processus de manière fondamentale et que l'on valide les modèles/bases de données utilisés pour de nombreuses méthodes, que comprennent éventuellement des études d'analogies avec la nature.

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## **1**        **INTRODUCTION**

### **1.1**      **Prolegomena**

This report presents a synthetic overview of the geochemistry of the near-field of a repository for vitrified high-level waste (HLW) located in deep sedimentary formations in Northern Switzerland (Nagra, 1988). It is based on a previous analysis for a crystalline host-rock (McKinley, 1985) carried out as part of the Project Gewähr 1985 (PG'85) safety analysis (Nagra, 1985). Discussion thus concentrates on the extent to which the far-field hydrology and geochemistry of the sediments may affect near-field performance.

### **1.2**      **Host-rock definition**

Areas of argillaceous sediments potentially suitable for HLW disposal are found in central and northern Switzerland (Nagra, 1988). By balancing depth of disposal (increasing isolation from the environment) with engineering practicality and temperature constraints, a repository depth of approx. 850 m below surface has been specified for the study. Applying further constraints of required formation thickness, areal extent, distance from major tectonic zones, etc., 2 preferred formations have been identified - the Opalinus clay (OPA) and the lower fresh-water Molasse (Untere Süswasser Molasse - USM). The USM is more extensive and thicker than the OPA (which may be only  $\approx 100$  m thick). USM is, however, somewhat heterogeneous (with extensive sand channels) and is therefore more difficult to model. Although much of the discussion will be fairly generic, OPA will be assumed as the reference formation. USM will be explicitly mentioned only when it would be expected to differ significantly from OPA due, for example, to differing hydrology or hydrochemistry.

The main mineralogical components of OPA and USM are listed in Table 1 and reference porewaters for these formations are presented in Table 2. As water flow in crystalline rocks tends to occur along clay filled fractures, the differences in aqueous geochemistry between these and argillaceous options tend to be rather small although, for example, the expected higher organic content of the latter can be very important. For the specific case of the near-field, the potential vulnerability of argillaceous rocks to alteration due to heating, drying or oxidation must also be considered.

**Table 1:** Mineralogy\* of the OPA and USM (Wittwer and McKinley, 1989)

<b>A</b> Major Mineralogy	OPA (wt %)	USM (wt %)	
		Sand	Clay
Calcite	9	20	20
Dolomite	-	2	2
Siderite	4	-	-
Ankerite	<1	-	-
Quartz	18	28	2
Feldspars	1	30	5
Clay/Accessory	65	≈13	≈70
<b>B</b>			
Accessory Minerals			
Pyrite	1.5		<1
Fe oxyhydroxide	trace		trace
Organic carbon	0.7		≈0.1
<b>C</b>			
Clay Mineralogy (% clay)			
Illite	45		60+
Kaolinite	25		10
Smectite	-		20
Chlorite	15		15
Illite/Smectite	15		-

\* Average values from ranges specified by the University of Berne, hence totals deviate from 100%

+ USM shows variation in clay mineralogy between regions west and east of the Lake of Zurich/Aare border. Values given are for the eastern region

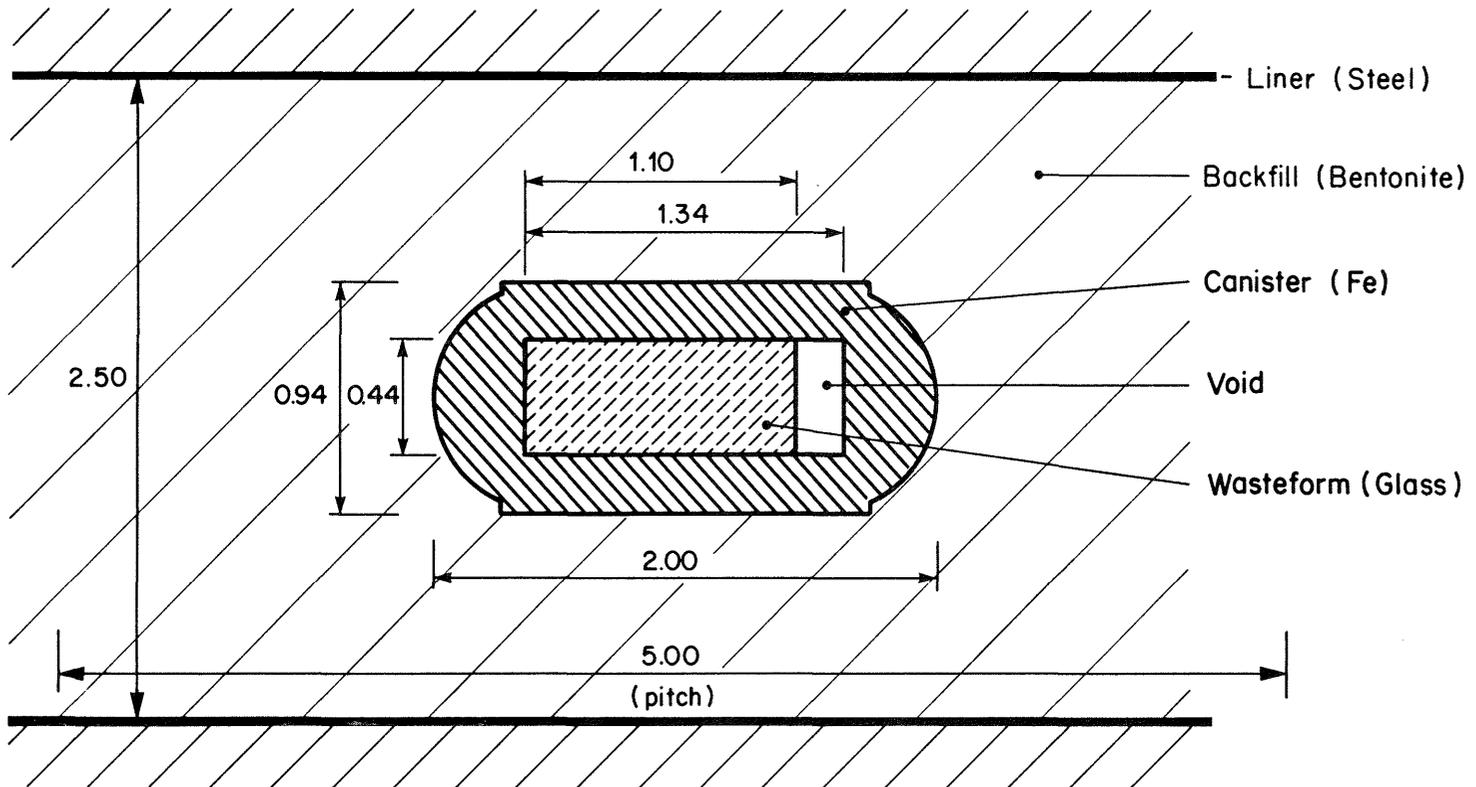


Fig. 1: Waste emplacement geometry (dimensions in metres)

**Table 2:** Reference Groundwaters (Wittwer and McKinley, 1989)

	OPA	USM	PG'85 crystalline
Temperature (°C)	45	40	55
pH	8.5	7.5	6.8
pe	-5.0 (±1.0)	-4.0 (±1.0)	-2.5 (±1.5)
Major dissolved species (M)			
Na <sup>+</sup>	1.9x10 <sup>-1</sup>	1.9x10 <sup>-1</sup>	1.8x10 <sup>-1</sup>
K <sup>+</sup>	3.1x10 <sup>-3</sup>	5.0x10 <sup>-4</sup>	1.2x10 <sup>-3</sup>
Mg <sup>2+</sup>	1.6x10 <sup>-2</sup>	2.8x10 <sup>-3</sup>	1.1x10 <sup>-4</sup>
Ca <sup>2+</sup>	4.9x10 <sup>-5</sup>	4.2x10 <sup>-3</sup>	2.2x10 <sup>-2</sup>
Sr <sup>2+</sup>		2.0x10 <sup>-4</sup>	2.4x10 <sup>-4</sup>
NH <sub>4</sub> <sup>+</sup>		2.0x10 <sup>-4</sup>	
Cl <sup>-</sup>	2.0x10 <sup>-1</sup>	2.0x10 <sup>-1</sup>	1.9x10 <sup>-1</sup>
SO <sub>4</sub> <sup>2-</sup>	5.0x10 <sup>-5</sup>	5.0x10 <sup>-5</sup>	1.6x10 <sup>-2</sup>
[Fe]		1.1x10 <sup>-8</sup>	8.0x10 <sup>-6</sup>
[C*]	2.2x10 <sup>-2</sup>	1.9x10 <sup>-3</sup>	2.0x10 <sup>-6</sup>
[Si]	5.1x10 <sup>-4</sup>	4.2x10 <sup>-4</sup>	2.7x10 <sup>-4</sup>

\* total carbonate system

### 1.3 Layout of the near-field

As a reference case, the general layout of the near-field will be assumed to be similar to that in PG'85 (Fig. 1). The main components are thus the vitrified waste itself, a thin steel fabrication container, a thick cast steel canister and a massive bentonite backfill. The waste inventories in PG'85, evenly distributed over 5,895 waste packages (cf. Appendix I), are also assumed as a reference (equivalent to a 240 GWea nuclear power scenario).

Unlike the crystalline rock a tunnel in a sediment would not be self-supporting and hence some kind of liner would be required, at least for the operational phase. For the reference case it is thus tacitly assumed that such a liner could be withdrawn after waste emplacement. Such removable liners may, in fact, be impractical, in which case a relatively thin steel liner can be assumed. The consequences for such a liner, or other liner options, are discussed separately in Chapter 7. Also on grounds of practicality of construction, a smaller diameter tunnel is considered. Reference tunnel layout, dimensions and liner design were not specified during the sediment study and there are slight discrepancies between various support documents. In this report, a tunnel internal diameter of 2.5 m (with or without liner) is assumed with a tunnel spacing of 25 m (axis to axis).

As in the previous study, the near-field is taken to include not only the engineered barriers but also that portion of the host-rock

which is significantly perturbed by the presence of the repository. In any host-rock, mechanical or geochemical alterations due to induced stresses and temperature changes have to be taken into account. For argillaceous rocks, however, oxidation processes during the operational phase may be a very important additional phenomena and this is considered in Chapter 3.

#### 1.4 Post-closure evolution of the near-field geochemistry

As in the crystalline host-rock analysis, the evolution of the geochemistry of the near-field can be considered as occurring in a number of phases. In general, additional processes need to be considered for the argillaceous rocks only at fairly early stages of this evolution (e.g. host-rock oxidation); at longer times only the varying rates of processes (e.g. canister corrosion, nuclide transport) need to be considered. The main processes involved for the argillaceous rock are therefore:

- 1 Regions of the host-rock are drained, destressed and partially oxidised during the operational phases of tunnelling and waste emplacement (and, possibly, liner removal). Acidic waters may result from pyrite oxidation causing rapid corrosion of the liner and possible alteration/dissolution of minerals in the host-rock.
- 2 Water re-invades zones of the repository host-rock which have been partially drained during the operational phase. The hydrology of the host-rock begins to stabilise and the bentonite buffer begins to adsorb water and swell. The tunnel begins to collapse against the backfill after removal of the liner.
- 3 The gradual wetting of the buffer is coupled to spreading of radiogenic heat from the waste through the buffer. After a thermal peak, which occurs within the first few years, the temperature profile through the bentonite and surrounding rock gradually decays away over a period of several hundred years, in line with the decrease in thermal output from the waste. During the same time period, the bentonite becomes saturated and exerts a swelling pressure on the surrounding rock and the waste package. This swelling and creep of the host-rock seals any remaining "construction gaps" in the backfill structure.
- 4 Oxidation of the host-rock may perturb the chemistry of the initial water inflow into the near-field (e.g. pyrite oxidation to give low pH). In addition, from first wetting, hydrothermal alteration of backfill (e.g. montmorillonite to illite) will commence, the rate of which will be controlled by reaction kinetics (temperature dependent) and the rate of supply of particular solutes (e.g.  $K^+$  for the conversion above). Corrosion of the cast steel canister will occur, which will initially be oxic but quickly become anoxic as trapped air is used up. The rate of corrosion may be affected by the build-up of layers of solid reaction products (oxy-hydroxides) or by the limiting rate of supply of corrodents or loss of dissolved or gaseous products by diffusion through the backfill (corrosion rates may thus be

less in the presence of a steel liner).

- 5 After the canister has been corroded to a certain extent, it will fail mechanically and fluid will then contact the waste matrix. Even after canister failure, however, continued corrosion of unreacted Fe and buffering by corrosion products will exert an influence on the chemistry of the water in contact with the waste glass.
- 6 Corrosion of the vitrified waste will occur by a process of congruent dissolution with some associated precipitation of secondary mineral phases. Preferential leaching of particular nuclides occurs in the very early stages of corrosion. During steady-state leaching, the rate of release of specific nuclides would be controlled either by the rate of glass matrix dissolution or by limits set by the total solubility of the element in question.
- 7 The leachate thus formed is transported to the far-field by diffusion through the remnant canister and corrosion products and the bentonite backfill. The rate of such transport will be dependent on diffusion rates in the bentonite pores, the magnitude of retardation processes occurring (e.g. sorption, ultra-filtration, ion-exclusion, etc.) and on the water flow field in the host-rock around the emplacement tunnels. The resultant radionuclide release rates provide the input functions for the far-field transport calculations. If flow in the far-field is heterogeneous on a scale of metres (e.g. localised fissures or sand channels) or, indeed, is so low that diffusive transport predominates, this should be taken into account.

A diagrammatic representation of the various components of the near-field and the dominant reactions occurring is presented in Fig. 2.

The following chapters consider these processes in more detail. In this treatment, the caveats discussed in detail by McKinley (1985) also apply, i.e.:

- 1 Individual processes are usually considered in isolation although, in reality, they are often competitive or synergistic. Such coupling is discussed in terms of the conservatism of the overall treatment but, as yet, no methodology exists to rigorously model all coupled processes in the near-field
- 2 The near-field is considered around a single canister and simply scaled up to derive total repository releases
- 3 Only a base case scenario of a homogeneous, smoothly evolving system is discussed without consideration of, for example, major disruptive perturbations
- 4 Hydrologic and geochemical conditions in the far-field are assumed to be constant
- 5 The effects of microbial contamination, organic complexants and colloids are not considered in the base case but are discussed separately in Chapter 7.

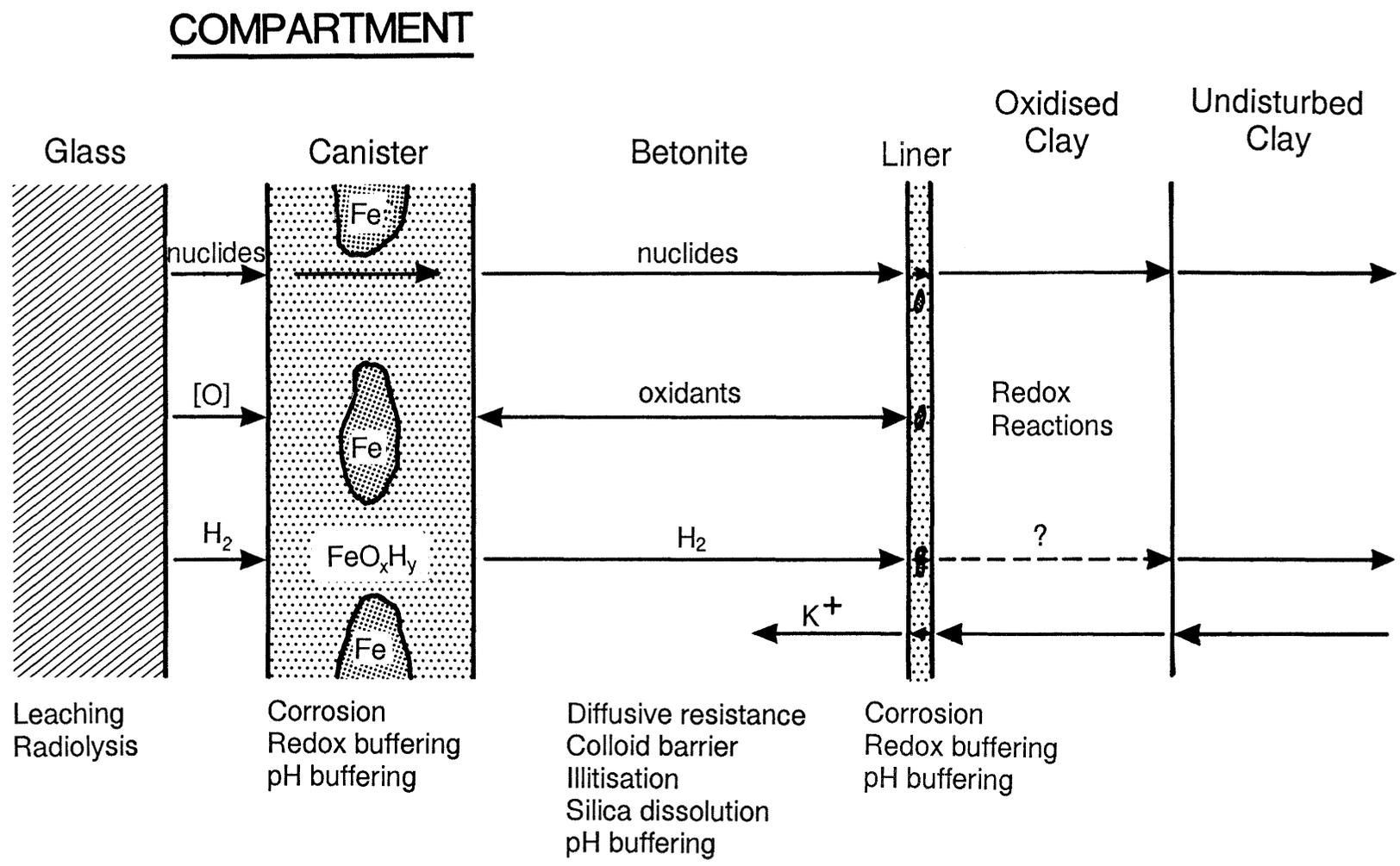


Fig. 2: Schematic diagram of geochemical processes in the near-field (not to scale)

## 2 NEAR-FIELD TEMPERATURES AND HYDROLOGY

### 2.1 Temperatures

To allow comparison with PG'85, this study has to take into account some important differences between the thermal properties of the crystalline and argillaceous host-rocks:

- a) **Ambient temperature** - due, primarily, to the lesser depth, an ambient temperature of approx. 40-45°C is expected in the sediments as opposed to 55°C for the crystalline.
- b) **Thermal conductivity** - is lower for clays,  $\approx 3 \text{ Wm}^{-1}\text{K}^{-1}$  for OPA and  $2-3 \text{ Wm}^{-1}\text{K}^{-1}$  for USM (Nagra, 1988) as opposed to a value of  $3.0-3.5 \text{ Wm}^{-1}\text{K}^{-1}$  which would be more likely for a granite (Hopkirk et al., 1983). It should be noted, however, that for the PG'85 reference near-field calculations a very conservative conductivity of  $2.5 \text{ Wm}^{-1}\text{K}^{-1}$  was used (Hopkirk and Wagner, 1986). The volumetric heat capacity is also likely to be slightly lower for the clay (i.e.  $2-2.2$  for OPA and  $1.9-2.2$  for USM as opposed to  $2.3 \text{ MJm}^{-3}\text{K}^{-1}$ ).
- c) **Higher water content** - which may decrease considerably during the operational phase. For OPA with an average porosity of 5%, this may not greatly alter thermal properties. For USM, with open porosity ranging from 3-21%, drainage could cause a considerable decrease in thermal conductivity and also a small decrease in heat capacity, especially in sand-rich zones. The variation of water content will be a complex function of resaturation from outside and drying from inside (due to radiogenic heat) and thus the disturbed far-field could, in principle, be treated in a similar manner to the bentonite backfill.

Calculations to date (Hopkirk and Zuidema, 1988) have considered only two extreme cases of a fully saturated bentonite/host-rock (conductivity =  $1.6 \text{ Wm}^{-1}\text{K}^{-1}$ , heat capacity  $2.0 \text{ MJm}^{-3}\text{K}^{-1}$ ) and a pessimistic unsaturated case ( $0.6 \text{ Wm}^{-1}\text{K}^{-1}$ ,  $1.8 \text{ MJm}^{-3}\text{K}^{-1}$  respectively). The results of these calculations are summarised in Table 3. It is clear that the unsaturated case results in a considerably longer high temperature phase ( $T > 100^\circ\text{C}$ ) in the near-field.

The build-up of the temperature profile and the resaturation of the host-rock/saturation of the bentonite during the early, high temperature phase are strongly coupled in a thermodynamic sense (Carnahan, 1989). As discussed above, the thermal properties of the clays are greatly influenced by their degree of saturation. The internal heat source, in turn, causes drying from the inside while resaturation from the outside is occurring, giving a complex 2 phase (liquid + vapour) flow system (possibly further complicated by water consumption and gas production from canister corrosion reactions - cf. Chapter 4). Such coupled systems are extremely difficult to model (Pruess, 1989), and even the decoupled

resaturation case (no temperature gradient) shows significant variations in calculated saturation time (from less than 100 to more than 1000 years) depending on assumptions made in geometry, hydraulic properties etc. (Andrews et al., 1986).

More realistic modelling, therefore, would reduce calculated temperatures from the very pessimistic case. If, nevertheless, lower near-field temperatures were considered advantageous, this could be assured by repository design (e.g. increasing canister pitch) or planning (decreasing waste loading in the glass or increasing surface cooling times prior to disposal). The effect of increased surface storage time can be quite considerable - for example, a change in the storage time from 30 to 50 y decreased the maximum tunnel wall temperature by 30°C in the Hopkirk et al. (1983) base case. In principle, therefore, the reference case 50 y storage assumed in this study could be further extended.

**Table 3:** Results of thermal calculations\*

Position	Clay (saturated)	Clay (unsaturated)	Crystalline
Glass centre	164 [70]	212 [180]	195 [80]
Canister/bentonite interface	137 [55]	185 [155]	153 [50]
Bentonite/host-rock+ interface	87 [--]	136 [105]	76 [--]

\* given as maximum temperature (°C) [time when T drops below 100°C following the thermal transient (years after emplacement)]

+ at r = 1.25 m for clay and r = 1.85 m for crystalline

Refs. - Clay: Hopkirk and Zuidema, 1988  
 - Crystalline: Hopkirk and Wagner, 1986.

## 2.2 Near-field hydrology

For the near-field analysis, two main hydrologic parameters are required - the total flux of groundwater through the repository and the spacial distribution of this flux with reference to the tunnel layout. In an ideal plastic clay formation, solute transport would occur predominantly by diffusion and advective transport could be considered negligible. In such a case, the entire formation would have properties generally similar to the bentonite backfill and a few tens of metres of undisturbed rock would act as a total barrier for all radionuclides over any sensible timescale (approx. 10<sup>6</sup> to

10<sup>7</sup> years; Baetsle et al., 1985; Chapman and Tassoni, 1985). Unfortunately, Swiss sediments cannot be considered ideal as they are known to contain significant fracture systems and, in the USM, highly conductive sand lenses and channels. Although it is not known to what extent such features are hydraulically active at appropriate depths, it must currently be assumed that they can act as preferential flow paths.

The regional hydraulic models used in the sediment study were shown to be very sensitive to data input, leading to considerable uncertainties in the expected water flux through the repository (Nagra, 1988). Base case values selected for hydraulic parameters are presented in Table 4 along with the equivalent data for the PG '85 crystalline. The "flux per canister" presented in this table is simply derived by dividing the flux through the entire repository area ( $\approx 0.74 \text{ km}^2$  for the sediments and  $\approx 1.36 \text{ km}^2$  for the crystalline) by the number of canisters ( $\approx 6000$ ). The assumption is that this flux, flowing through  $\approx 125 \text{ m}^2$  of rock ( $\approx 200 \text{ m}^2$  for crystalline), can exchange solutes with the near-field. Such an assumption is obviously very simplistic and could involve over-prediction of the effective flux.

**Table 4:** Assumed base-case hydraulic parameters

Parameter	OPA	USM	Crystalline
Average conductivity (m/s)	$10^{-12}$	$10^{-2}$	$10^{-11}$
Hydraulic gradient (m/m)	0.1	0.01	0.012
Average flux (l/m <sup>2</sup> .a)	$3 \times 10^{-3}$	$3 \times 10^{-2}$	$4 \times 10^{-3*}$
Flux per canister (l/a)	0.4	4	0.7*

\* for assumed 70° flow vector - cf. Nagra, 1985.

In order to properly assess solute exchange with the near-field, however, the small scale distribution of flow must also be defined. With preferential flow in sub-vertical planar features perpendicular to the tunnels (Fig. 3a), the fraction of the total water flux "exchanging" with the near-field will depend on the extent of the decompressed zone but might be  $\approx 20\%$  of the total flux (considering the geometry of 2.5 m diameter tunnels at a spacing of  $\approx 20 \text{ m}$ ). This exchange would, however, be localised to the point of intersection with the tunnel unless significant flow also occurred along the tunnels in the decompressed zone. In the case where the sub-vertical fissure runs along the tunnel,

effectively 100 % of the flux might exchange but, apart from the fact that tunnel layout should actively avoid such features, the probability of a particular tunnel being close to such a feature would depend on the fissure spacing.

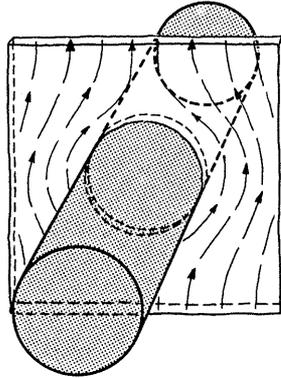
Much more extensive exchange of solute from flowing water with the near-field would occur in the case of flow in horizontal features such as sand layers (cf. Fig. 3b). In this case, however, it is less reasonable to consider the canisters independently and effects such as depletion of active groundwater constituents (e.g. oxidants) and saturation of radionuclides in the water contacting "downstream" canisters should be evaluated. Although ignoring these particular processes would be "conservative", the possible existence of any "domino effects" would have to be checked although, for the specified disposal option, none are immediately obvious.

The final case of preferential flow is in sand channels in the USM. Although flow in this case is very localised (and hence the net effect on the majority of the waste canisters is negligible), a consequence of such localisation could be relatively high water velocities which could possibly lead to problems of backfill erosion.

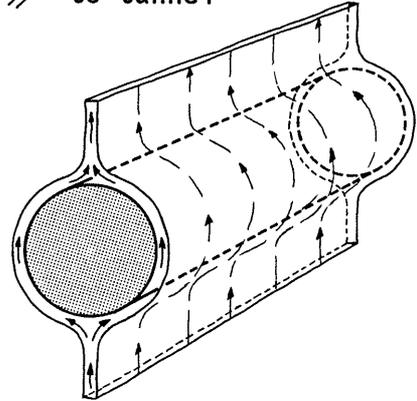
In most of the following sections, solute exchange will be evaluated by using the base-case flux per canister. The consequences of preferential flow in distinct features will, however, be discussed further in Chapter 7.

a) Sub-vertical fissure

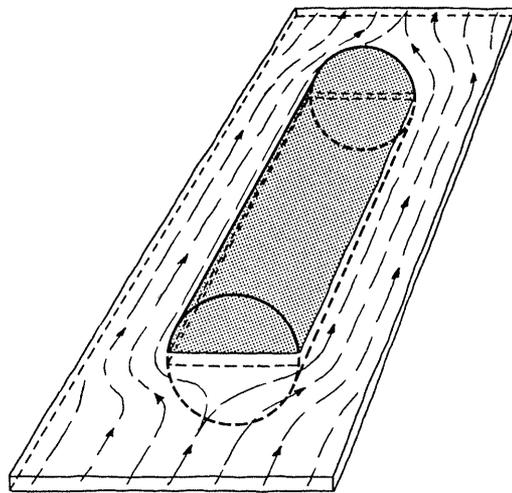
Fissure  $\perp$  to tunnel



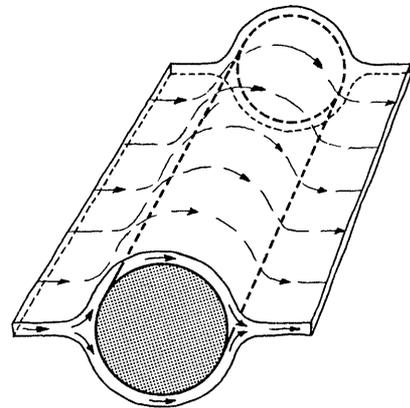
$\parallel$  to tunnel



b) Horizontal fissure/sand layer



Flow  $\parallel$  to tunnel



Flow  $\perp$  to tunnel

c) Sand channel

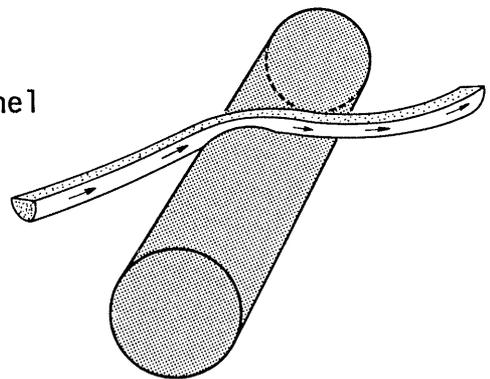


Fig. 3: Preferential flow in the near-field

### 3 BACKFILL AND THE DISTURBED ZONE

#### 3.1 Evolution of the disturbed zone

The process of tunnelling inevitably causes stress relief in the adjacent rock with potential increase of hydraulic conductivity. This decompressed zone is typically anisotropic and is generally taken to extend 1 to 2 tunnel radii from the wall (Kelsall et al., 1984). In plastic clay, destressing effects may be measured as far as 5 tunnel radii distant from the axis of the excavation (Neerdael and Debruyne, 1988). During operation of the repository, pumping and ventilation will drain some of the surrounding rock and the decompressed zone will be particularly vulnerable to this process. It may be noted that, while tunnel linings may hinder this process, any major conductive features intercepted (e.g. sand channels) may extend the drained zone.

When clays are dried, intralamellar water can be removed irreversibly causing changes in physical properties (e.g. swelling capacity) which could prevent recovery of the original conditions in the rock following resaturation. For the reference case, however, when temperatures outside of the emplacement tunnel remain <100°C, such intralamellar drying would not be significant (Grauer, 1986) and thus this effect can be ignored.

Potentially much more important, however, is the penetration of air into the drained rock with associated oxidation of susceptible minerals (especially pyrite). Although the oxidation of pyrite is rather slow kinetically in low-temperature inorganic systems, it is readily catalysed by microorganisms (Grogan, 1987) and can be fast in damp clay systems exposed to air (Baeyens et al., 1985). A typical net oxidation reaction would be



i.e. production of 2 moles of sulphuric acid for each mole of pyrite oxidised. This acid will be buffered in the sediments, to some extent, by reactions such as calcite dissolution, e.g.



Given the presence of sulphate, any such dissolved calcium may precipitate as gypsum. At higher temperatures, additional dissolution of Mg carbonates (e.g. Dolomite -  $\text{CaMg}(\text{CO}_3)_2$ ) together with the greater solubility of  $\text{MgSO}_4$  results in the formation of groundwater enriched in Mg and  $\text{SO}_4$  (Krumhansl, 1986). Another sulphate mineral which commonly forms during pyrite oxidation is jarosite -  $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$  (Lowson, 1982; Baeyens et al., 1985) - which may also act as a pH buffer.

In lower temperature systems, persistence of low pH (< approx.4) is often observed despite the presence of considerable quantities of carbonates in the system (e.g. MacKenzie et al., 1983). Pyrite

oxidation may be localised and biogenic micro-environments with very low pH may form, which would encourage other buffering reactions, e.g.



or, indeed, aluminosilicate mineral dissolution. All of the processes considered above (acid formation, carbonate dissolution/sulphate precipitation, carbon dioxide gas formation, silicate (or other) mineral dissolution) would complicate the geochemistry and physical properties of the drained zone. Additionally, resultant changes in the porewater in this region could affect the performance of engineered barriers (cf. Rainey and Rosenbaum, 1989).

In order to quantify the expected extent of the disturbed zone, information is required not only on the rate of penetration of oxidant into the rock during the operational phase and the duration of this phase, but also on details of the oxidation mechanism. In the following discussion it is assumed that there is a ready supply of the water required for the pyrite oxidation. If water transport rates are very low - which may be the case if most of the porosity is filled with "geo gases" (e.g.  $\text{H}_2$ ,  $\text{CH}_4$ ) - this may considerably limit the rate of pyrite oxidation.

Taking the disturbed zone to extend one tunnel radius from the wall (1.25 m), this would correspond to a rock volume of  $\approx 74 \text{ m}^3$  per canister. For OPA with a pyrite content of 1.5 %, such a volume would contain  $\approx 2.8 \times 10^6 \text{ g}$  of  $\text{FeS}_2$  equivalent to  $\approx 2.3 \times 10^4$  moles. From reaction (1) above, complete oxidation of this pyrite would require  $\approx 8.6 \times 10^4$  moles of  $\text{O}_2$  equivalent to  $1.9 \times 10^3 \text{ m}^3$  (STP). Assuming that tunnels lie open for 10 years, such an oxygen input would require a flux of  $\approx 10^{-5}$  moles/ $\text{m}^2$ /sec over the tunnel surface ( $\approx 25 \text{ m}^2$  per canister). This flux is much larger than can be supported by diffusion of dissolved oxygen in water - such a mechanism would cause complete oxidation of a layer only  $\approx 1 \text{ mm}$  thick in 10 years (Cathles, 1982; cf. Fig. 4). It can be noted from Fig. 4 that  $\text{Fe}^{3+}$  can act as more efficient oxidant in such systems if the pH drops, and has been postulated to be the main pyrite oxidant in acid mine drainage studies (Cathles, 1982; Moses et al., 1987). Nevertheless, within a period of 10 years the thickness of rock which could be oxidised by oxidant diffusion would not be more than a couple of centimetres. Figure 4 also illustrates, however, the dramatic increase in oxidation rate if diffusion of air into open pores can occur. The smaller pores will remain water filled and support a flux of water towards the tunnel driven by the relatively high hydraulic gradients in the immediate vicinity and the effects of surface drying due to ventilation (capillary suction). Larger pores and fissures, however, may well be drained - especially within the mechanically disturbed zone - giving rise to a connected air-filled porosity. Quantitative evaluation of development of such an unsaturated system, and transport within it, is extremely complex (Pruess, 1989) but the simple estimates by Cathles (1982) shown in Fig. 4 indicate that oxidation of a layer a metre or more thick

within 10 years could be expected. If unsaturated conditions occur, therefore, it is not unreasonable to expect complete oxidation of the disturbed zone, previously taken to extend one tunnel radius out from the drift wall. Combining oxidant transport in air-filled pores with solution-phase  $\text{Fe}^{3+}$  diffusion would allow fairly homogeneous oxidation as long as open pores/fractures were not separated, on average, by more than a few centimetres.

In order to evaluate the consequences of such pyrite oxidation, the detailed mechanism has to be known. The first stage of pyrite oxidation may well be incomplete, particularly when catalysed by  $\text{Fe}^{3+}$ , and be better represented by an equation such as



where the  $[\text{S}_2^{2-}]$  may react further to form polysulphides or, as often observed, elemental sulphur (Lowson, 1982). This oxidation is usually microbially catalysed (Cathles, 1982) but, although the detailed reaction is thus difficult to specify, it is clear that such partial oxidation would consume about an order of magnitude less oxygen per mole of pyrite oxidised than the complete oxidation represented by equation (1) above. In such a case, the rate of oxidation would be about an order of magnitude faster if transport of oxidant was the limiting factor.

Such incomplete oxidation has been postulated to occur in marine sediments (Berner, 1980) and at the Osamu Utsumi uranium mine, studied as part of the Poços de Caldas natural analogue study (Smellie et al., 1989). Microbially catalysed pyrite oxidation at this site produces an aqueous sulphur species which is not identified by current analytical protocols (which include sulphide and sulphate) and has been assumed to be either polysulphides or colloidal sulphur. This sulphur species is further oxidised to sulphate by sulphur-oxidising bacteria only in surface waters where rapid acidification occurs, leading to pH values  $\approx 2$  (West et al., 1989).

From the information above, it is possible to postulate a number of scenarios for host-rock oxidation:

- i) The disturbed zone remains saturated; oxidation occurs only to a depth of a few centimetres at most, acid produced is buffered by the calcite content ( $\approx 9\%$  by weight in OPA) with some minor formation of sulphate minerals (e.g. gypsum, jarosite). Alternatively, any unsaturated porosity is filled with reducing formation gas (e.g.  $\text{H}_2$  or  $\text{CH}_4$ ) which limits penetration of air.
- ii) The disturbed zone becomes unsaturated and complete oxidation of pyrite occurs in this region. Balancing reactions (1) and (2) above would indicate that a major part of the inventory of

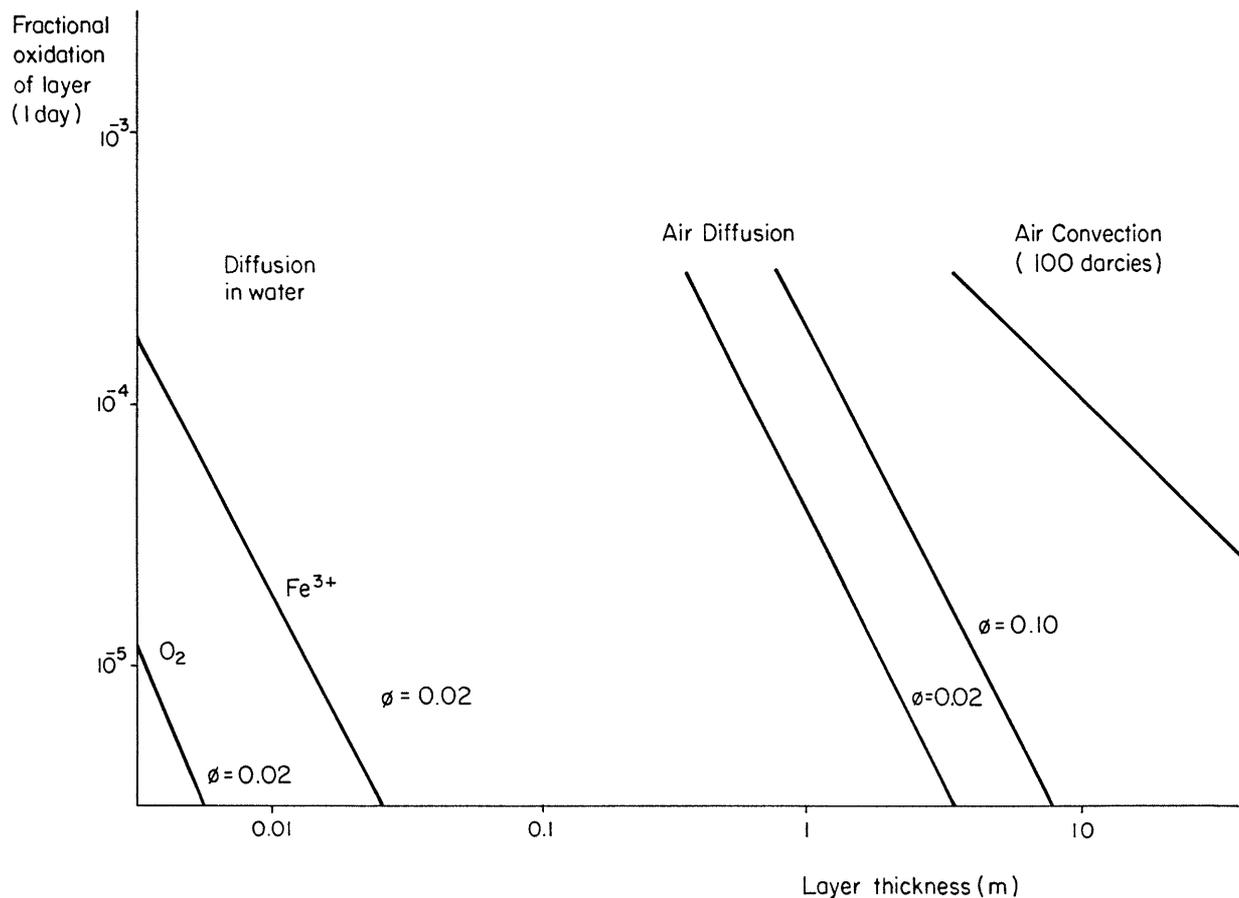


Fig. 4: Oxidation rates for pyrite due to various oxidant transport mechanisms (derived from Cathles, 1982). The graph shows the rate of oxidation of a rock containing finely dispersed pyrite (2 % by weight) based on diffusion calculations assuming a linear concentration gradient over the layer considered, boundary conditions of saturation of  $O_2$  in water and an  $Fe^{3+}$  concentration of 1000 ppm, and complete oxidation of the pyrite (cf. equation (1) in text). Three cases of oxidant transport are considered:

- diffusion in water, porosity 0.02,  $O_2$  and  $Fe^{3+}$  calculated separately
- $O_2$  diffusion in gas-filled pores, porosity of 0.02 and 0.10
- air convection.

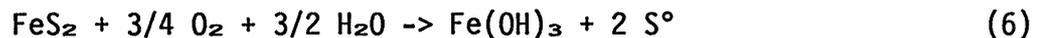
calcite could be consumed by buffering reactions (>50% for OPA) giving significant mineral alteration throughout this region. Very low pH values would not be expected, however, precluding consequent aluminosilicate degradation.

- iii) The disturbed zone becomes unsaturated but oxidation is incomplete. Reaction (4) indicates, however, that acid production is still fairly extensive and hence significant calcite dissolution is to be expected. The aqueous sulphur species (represented simplistically as  $[S_2^{2-}]$ ) would be transported in the net water flux towards the tunnel wall where it would be further oxidised, e.g.



Although the actual oxidation reaction may be somewhat different, the net result is that a major part of the acid formation (and most of the sulphate formation) occurs at the tunnel wall. At this location, pH may drop to values approaching 2 resulting possibly in pooling of acidic waters and extensive mineral alteration (including aluminosilicate degradation).

It can be noted that, as a worst case, the overall oxidation can be separated into two steps:



(in the bulk rock)



(at the tunnel wall)

where all of the acid production would be localised at the tunnel wall.

The consequences of the various alteration scenarios in terms of their influence on near-field hydrology will be considered further in Chapter 7. In the following sections only the chemical effects of such alteration will be considered. In the case of complete oxidation, this will predominantly result in the alteration of pyrite to ferric hydroxide (or oxyhydroxide) and calcite (or other carbonates) to gypsum (or other sulphates). In the case of incomplete oxidation, pyrite to ferric oxyhydroxide conversion and calcite leaching will occur in the bulk rock while acid buffering reactions and sulphate formation will occur at the tunnel wall. At the latter location, typical buffering reactions might include leaching of Al from aluminosilicates (Baeyens et al., 1985) with associated degradation of clay minerals. An example of such a reaction is the dissolution of kaolinite (Stumm and Morgan, 1981) which could be represented by the equation:



A further important reaction could be corrosion of the steel liner, which would be very fast at low pH, i.e.:



The low pH may also cause flocculation of the dissolved organic carbon (except for the smallest fulvic acids) leading to localised build-up of organic material.

Finally it should be noted that additional alterations of the host-rock would occur - in particular oxidation of organic carbon. Such reactions would be slow without organic catalysis and are considered further in Chapter 7.

After filling and sealing of the emplacement tunnel, any oxygen in the trapped air in the system will be used up and the oxidised zones will re-equilibrate with reducing formation water. Any low pH regions will be buffered or flushed out, minerals which are unstable in this water regime may be transformed (sulphate dissolution with subsequent re-precipitation of carbonates or sulphides). The time period taken to re-establish the water chemistry may be much longer than the period for which the system was oxidising. For example, 74 m<sup>3</sup> of OPA around a single canister could contain over 4.6x10<sup>4</sup> moles of freshly precipitated gypsum if all sulphuric acid production was balanced by the calcite to gypsum reaction. Thus, even though the OPA reference water is considerably undersaturated in gypsum, the water contacting the tunnel wall could be saturated in this mineral for periods on the 10<sup>6</sup> year timescale (0.4 l/canister.year dissolving 2x10<sup>-2</sup> moles/l gypsum to reach saturation).

For USM, with a lower pyrite content and higher calcite content relative to OPA, the consequences of complete oxidation are likely to be less marked. Sandy structures, however, may become more readily unsaturated and provide a more extensive porosity for gaseous oxygen diffusion. If the oxidation reaction is incomplete and reduced S species are transported towards the tunnel, a similar problem with acidification at the tunnel wall could be expected (N.B. particular association of acidification effects due to pyrite oxidation with sand-rich zones has been reported - Rainey and Rosenbaum, 1989).

### 3.2 Host-rock/backfill interface

Assuming the liner is removed, on closure compacted bentonite is in contact with oxidised sediment, possibly containing low pH pore-water. Initial creep by the sediment, followed by swelling of the bentonite as it begins to saturate, will ensure intimate contact between backfill and host-rock in the interface region. If acidification of the host rock is negligible, the basic similarity of the host rock and the bentonite would argue against any significant geochemical gradients in this region or extensive rock/backfill interaction.

During this initial period, temperatures will be high - peaking at over 150°C at the canister/ backfill interface (cf. Table 3). Although the water content of the bentonite is fairly low at this time, such temperatures are known to cause the porewater pH to decrease considerably (Johnston and Miller, 1984), without, however, significant alteration of the bentonite structure and physico-chemical properties. The flow of low pH groundwater from the oxidised zone beyond the tunnel wall might not, therefore, be expected to cause drastic perturbation of the overall system in any case. On the other hand, experiments in acidic media at  $\approx 25^\circ\text{C}$  indicate that smectites are very unstable at  $\text{pHs} \leq 3-4$  and may dissolve totally (May et al., 1986). In the face of such contradictory evidence, it must be assumed that such low pH conditions would be detrimental to bentonite stability.

As the temperature drops, the pH will rise due to the overall buffering by the bentonite and, by the time temperatures are close to ambient (approx. 200 to 500 years), the pH will be expected to be buffered back to the neutral/alkaline region (cf. next section). The increased concentration of some cations (e.g.  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ) in the acidic leachate from the pyrite oxidation may cause displacement of exchangeable ions (mainly  $\text{Na}^+$ ) on the bentonite. Quantitative analysis of this interface is, however, very dependent on the performance of the liner and, hence, will be discussed further in Chapter 7.4.

### 3.3 Bulk Bentonite

Given that the reference sediment groundwaters are, in essence, very little different from the PG'85 crystalline groundwater chemistry (cf. Table 2), the backfill would be expected to be similarly stable. In fact, given the presence of montmorillonite type minerals (smectites) in the host-rock, dissolution of bentonite minerals is not expected to be significant and the predominant mechanism of interest would be clay mineral conversion. Both the presence of extensive smectite in the surrounding host-rock and the low temperatures ( $\leq 100^\circ\text{C}$ ) during the period in which the bentonite is resaturated argue against montmorillonite to illite conversion being important (cf. McKinley, 1985; Pusch, 1985). Nevertheless if, as in PG'85, kinetic influences are neglected, the main factor influencing this transformation is the rate of supply of  $\text{K}^+$ . Although the data are somewhat uncertain, the reference OPA and USM waters have  $\text{K}^+$  concentrations differing by a factor of 6, the former 3 times more and the latter 2 times less than the PG'85 water (Table 2); this is compensated by the fact that the base case groundwater flux is 10 times higher for USM than OPA. As the bentonite inventory around a single canister is approx. half that in PG'85 (23 as opposed to 53  $\text{m}^3$ ), the bentonite "lifetime" with respect to illitisation would be about  $10^7$  years for total conversion in both the OPA and the USM system (assuming  $3.0 \times 10^4$  kg of montmorillonate/canister and a requirement of 50 meq  $\text{K}^+$ /100 g for conversion - cf. McKinley, 1985).

A number of other alteration reactions have been considered (e.g. chloritisation) but, despite the rather poor quality of thermodynamic and kinetic data, there is a consistent picture indicating very long term stability of bulk bentonite under repository conditions (cf. reviews by Grauer, 1986; 1988). This conclusion is supported by numerous studies of natural analogues (e.g. Pusch et al., 1987).

Although the bulk mineralogical stability of the bentonite seems reasonably assured, the constancy of physico-chemical parameters is not so well established. Following the work of Couture (1985), there is particular interest in the rapid loss of bentonite swelling pressure after contact with steam at temperatures between 150 and 250°C. This phenomenon seems to result from cementation by silica which appears to occur more rapidly in unsaturated rather than saturated conditions (Pusch 1987; Pusch and Güven, 1988). This process is temperature dependent and appears to be measurable down to temperatures of 100°C - at least for unconsolidated samples (Oscarson et al., 1988). Evidence for such cementation has also been seen in natural systems (Pusch and Karnland, 1988b).

In order to evaluate the consequences of such loss of swelling pressure, the various rôles of the bentonite backfill need to be considered. These require the properties of

- i) plasticity and swelling capacity - to ensure sealing of all construction gaps allowing the bentonite to be treated as a homogeneous mass. Such plasticity also allows minor earth movements to be accommodated without disruption of this barrier.
- ii) low hydraulic conductivity - ensuring that solute transport occurs predominantly by diffusion
- iii) small pore size - preventing transport of colloidal-sized particles
- iv) stiffness - preventing the canister from sinking through the bentonite.

As noted by Grauer (1988), indications to date are that at least at lower temperatures ( $\leq 150^\circ\text{C}$ ), sufficient swelling properties would remain to ensure that the bentonite can be considered as plastic with a sufficiently low permeability. Such a conclusion is well supported by detailed studies of natural, hydrothermally altered bentonites and smectite rich clays (Pusch et al., 1987, Müller-Vonmoos et al., 1988).

Of more concern, however, are microstructural studies which indicate that agglomeration of montmorillonite flakes with resultant formation of larger voids occurs during heat treatment, particularly under unsaturated conditions (Pusch, 1987; Pusch and Karnland, 1988a). Although such clumping seems to be reversible up

to  $\approx 150^\circ\text{C}$  (Pusch and Karnland, 1988), the formation of a connected network of larger pores would considerably affect the near-field release models used (cf. Chapter 6.1). In particular, this could undermine the very important rôle of the bentonite as a colloid filter. Even though such pores would diminish any possible problems from gas production (cf. Chapter 4.3), it can be concluded that their presence would be generally undesirable and should be avoided by ensuring that temperatures remain below  $150^\circ\text{C}$ .

Finally, it may be noted that the cementation reactions would increase stiffness and hence decrease the rate of canister sinking (cf. Pusch et al, 1987; Pusch and Karnland, 1988a). This gain must be balanced against the fact that predicted sinking rates are, in any case, very low ( $\approx \text{mm}/10^6 \text{ y}$  - Pusch, 1983) and that further resistance to sinking can be achieved by use of sand-bentonite mixtures, as in the Canadian concept (Graham et al, 1988).

From the discussion of temperatures and resaturation in Chapter 2.1, it is clear that such thermal alteration processes are unlikely to be significant in the rapid saturation scenario presented, as the maximum temperatures in the bentonite stay below  $150^\circ\text{C}$  and, in much of the mass, below  $100^\circ\text{C}$ . In the unsaturated scenario, however, long duration of temperatures well above  $100^\circ\text{C}$ , even at the bentonite/host-rock interface, could cause significant alteration. Unless the potential problem of colloid transport could be better resolved - e.g. by direct studies on altered material - it may be necessary to ensure that such high temperatures do not occur. If such temperatures are not artefacts of over-conservative modelling (choice of parameters), design/operational alterations can be considered such as a) extending storage time prior to emplacement to decrease thermal output, b) changing the near-field geometry or c) increasing the thermal conductivity of the backfill (e.g. by adding silica sand - Radhakrishna, 1984) and the host-rock (by liner design to prevent draining during the operational phase).

Apart from its physical properties, in the Swiss disposal concept the bentonite also acts as an important buffer of the near-field chemistry. Empirically, smectites are known to buffer pH in aqueous slurries in the mildly alkaline region ( $\approx \text{pH } 9$  for Na smectite - Johnston and Miller, 1984), which is explained in terms of proton ion-exchange reactions. Wanner (1986) has proposed an ion-exchange model which predicts that higher pH values (up to about 9.6) could be caused by Ca for Na ion exchange and associated calcite dissolution (giving also a consequent increase in alkalinity). Such a model is, however, inherently limited by the fact that it considers neither  $\text{Na}^+/\text{H}^+$  ion exchange nor mineral alteration reactions (cf. Grauer, 1988). The latter reactions become particularly important at pH values above about 9 due to the greatly increasing solubility of silica and alumina (Stumm and Morgan, 1981). At temperatures above  $100^\circ\text{C}$ , indeed, mineral dissolution reactions can cause a net decrease in pH - dropping into the mildly acid range ( $\approx 6$  - Johnston and Miller, 1984). Unfortunately, thermodynamic data on smectite dissolution are somewhat sparse and, indeed, the system may be inherently impossible to model by current techniques which cannot

handle the solid solutions which are important products (May et al., 1986; Grauer, 1988).

Given that no experimental data exist for reaction of sediment porewaters with Na bentonite at appropriate temperatures, a best guess of bentonite porewater pH in the OPA case in the range of 8.5-9 would have to be bounded by a wider conservative range - 7.5-10, say. Nevertheless, from the discussion above, pH values above about 9 must be considered to be rather unlikely.

The USM groundwater has a lower pH than that in the OPA but has a significantly higher Ca concentration (although still lower than that in the crystalline water). The "Wanner" ion exchange model would thus predict a larger pH rise for USM than OPA, tending to minimise differences in the porewaters resulting from the two groundwaters. The pH ranges assumed for OPA may thus also be considered reasonable for the USM. Increased calcite dissolution in the USM case would also increase the alkalinity - again making the porewater more similar to that from the OPA.

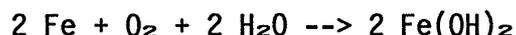
In addition to buffering pH, components of the bentonite may also play a role as redox buffers or clay surfaces may act as catalysts for equilibration between different redox couples (Laszlo, 1987). However, the canister is a more important redox buffer and this will be considered further in Chapter 4.3. The consequences of host-rock oxidation on bulk porewater chemistry are also considered in this section.

## 4 CANISTER CORROSION AND THE REDOX CONDITIONS IN THE NEAR-FIELD

### 4.1 Corrosion rates

Likely corrosion mechanisms for cast steel in the reference repository environment are (NWGCT, 1984):

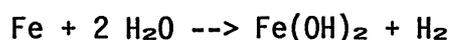
1 O<sub>2</sub> as electron acceptor (immediately post-closure)



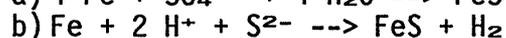
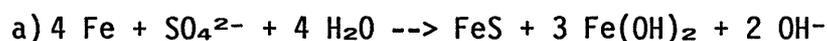
(conservative assumption; more reasonable is



2 H<sub>2</sub>O as electron acceptor: e.g.



3 SO<sub>4</sub><sup>2-</sup>/S<sup>2-</sup> (microbially catalysed)



Immediately post closure, canister corrosion will occur in an unsaturated environment containing trapped air. It is probably reasonable to consider that air trapped in the host rock can be ignored in this regard with oxygen consumed by corrosion of pyrite or the liner. Assuming reaction (1) to represent such corrosion and that all trapped oxygen is consumed by oxidation of the canister, an average corrosion depth of <0.7 mm was calculated for the PG'85 reference case (NWGCT, 1984). Scaling this calculation for the smaller volume of bentonite round each canister would predict ≤0.3 mm corrosion for the sediment case. Such a calculation does not take into account passivating layers which have been noted to form during corrosion of cast steel in air/steam at temperatures of 150 - 200°C (Lutton et al., 1987). Such layers greatly reduce corrosion and hence much of the trapped oxygen may be consumed by reaction with iron minerals in the bentonite or in the host-rock (or in the liner). Reported corrosion rates of ≤0.001 mm/year (Lutton et al., 1987) would result in an oxic period lasting ≈300 years if canister corrosion was the only oxygen removal mechanism - a period which may be comparable with the bentonite saturation time (cf. Chapter 2).

After resaturation, corrosion will proceed with either dissolved oxidants or water itself acting as oxidant. The rate of direct reaction with water, with consequent H<sub>2</sub> production, is mainly dependent on temperature and porewater chemistry (in particular, pH and redox conditions). Depending on the resaturation time and the assumed far-field thermal properties (cf. Table 3), the temperature when liquid water first contacts the canister surface may be either slightly above or below 100°C. Under such conditions, general corrosion rates ≈1-6 μm/a are to be expected (Marsh and Taylor, 1988). Sensitive measurement of H<sub>2</sub> production rates indicate that

such corrosion in typical crystalline groundwaters will be  $< 2.5 \mu\text{m/a}$  and would further decrease with increasing pH (Schenk, 1988).

In cases of anaerobic corrosion, it has been noted that even potentially aggressive anions such as  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  do not significantly affect rates, at least up to  $90^\circ\text{C}$  (Marsh and Taylor, 1988). In PG'85, however, an additional allowance of  $0.38 \mu\text{m/year}$  was made for corrosion due to  $\text{SO}_4^{2-}/\text{S}^{2-}$  from the bentonite (NWGCT, 1984). Although the sediment groundwater has a much lower sulphate content than the reference crystalline water (Table 2), host-rock oxidation could be assumed to ensure saturation in gypsum for the first few thousand years. Hence the PG'85 corrosion allowance for gypsum saturated groundwater could be directly applied to the sediment case.

From the data above, the 5 cm corrosion allowance would be expected, realistically, to last  $\approx 8000$  years (for  $6 \mu\text{m/a}$ ) after which the canister would fail mechanically. At this corrosion rate, metallic iron would be present for a further  $\approx 30,000$  years and, thereafter, the mass of corrosion products would continue to act as a redox buffer. It should be emphasised that uniform corrosion is not the only mechanism which can lead to canister failure. To allow for possible processes such as pitting or stress-corrosion cracking, a large safety margin is included in the calculations of canister lifetime. Even application of the very conservative PG'85 analysis (NWGCT, 1984) would predict penetration of  $< 3$  cm in 1000 years giving a minimum lifetime of  $> 1500$  years.

One factor considered only indirectly in reaction (3) above is the rôle of microbial activity in canister corrosion. As discussed in more detail in Chapter 7.1, the potential for microbial activity is much greater in the sediments than was the case in the crystalline. Marsh and Taylor (1988) discount the possibility of microbial colonisation of the canister surface on the grounds of temperature and radiation dose. Although the argument may be justified for aerobic organisms, the anaerobes such as the important sulphate reducing bacteria are known to be much more heat and radiation tolerant (West et al., 1986) and hence may well populate the canister as soon as temperatures drop sufficiently for liquid water to be present. When autotrophic (carbon fixing) organisms are present, organic carbon may not be the limiting factor (as assumed by Marsh and Taylor, 1988) and hence the key parameter would be the supply rate of  $\text{SO}_4^{2-}$ . Although the corrosion rate should, nevertheless, not exceed that previously estimated for  $\text{SO}_4^{2-}/\text{S}^{2-}$ , the potential use of other electron acceptors (e.g.  $\text{CO}_3^{2-}$ ) by such anaerobes should be investigated and the consequences evaluated. Microbiological effects are further discussed in Chapter 7.

## 4.2 The canister/backfill interface

Conservative calculations on the rate of H<sub>2</sub> production from anaerobic corrosion of steel indicate that potential problems could arise from gas build up (e.g. Neretnieks, 1985). Discussion of this for the crystalline case (cf. McKinley, 1985) indicated that any problems involved could probably be solved by engineering and such arguments should also be directly applicable to the sediment case.

Direct interaction between canister corrosion products and bentonite is expected at their interface forming iron silicates on the canister and iron rich clays (e.g. Fe-chlorite, Fe-chlorite-smectite - Grauer, 1988). While the former reaction would be protective (decreasing corrosion rates) the latter would probably encourage corrosion by removing Fe from corrosion layers. It is unlikely, in any case, that the net effect would significantly decrease estimates of minimum canister lifetime, especially in view of the conservatism involved in its assessment (cf. discussion in previous section). This is supported by empirical observation that corrosion rates decrease and pitting is absent in experiments performed with bentonite present (Marsh and Taylor, 1988).

One consequence of the Fe-rich clay formation, however, is the production of protons causing a net pH decrease (Savage, 1986) which could persist locally despite the considerable buffering capacity of the bulk bentonite. This process, together with pH buffering by Fe oxyhydroxide corrosion products to about 9.5 (Heusler, 1985; Marsh and Taylor, 1988), could give rise to a significant pH gradient over this zone. The steepness of this gradient will depend on buffering kinetics and the diffusivities of H<sup>+</sup> and OH<sup>-</sup>, which should be evaluated by, at least, scoping calculations.

The canister/backfill interface is also exposed to an enhanced n/γ radiation field but, due to shielding by the canister, the effects of this on corrosion or pH/redox conditions can be considered negligible (cf. McKinley, 1985). Following canister failure, α-radiolysis can be geochemically significant and is considered further in the next section.

## 4.3 Redox conditions

Apart from providing absolute containment for a set period, the canister has an additional rôle as a chemical buffer which it fulfils even after loss of mechanical integrity. Particularly important in this regard is the buffering of any oxidants produced by radiolysis. The calculation of maximum oxidant production (mainly from α-radiolysis of water, assuming all H<sub>2</sub> produced is chemically inert) presented for the PG'85 reference case (McKinley, 1985) is directly applicable. This indicates that <1 % of the canister mass (as Fe<sup>2+</sup>) would buffer all oxidant which could possibly be produced over a period of 10<sup>6</sup> years. Thus, even though all redox sensitive species in the glass matrix itself will be

oxidised, the leachate will be reduced by  $\text{Fe}^{2+}$  dissolving from the canister, with probable precipitation of secondary phases.

The canister corrosion will also buffer pH. At early stages of corrosion, amorphous  $\text{Fe}(\text{OH})_2$  dissolution may give rise to a  $\text{pH} \geq 9$ . As the corrosion products age, oxides such as magnetite ( $\text{Fe}_3\text{O}_4$ ) will form which could buffer pH in the range  $\approx 7$ -8.5, depending on temperature (Heusler, 1985). At host-rock ambient temperature, a pH of  $\approx 8$  might be expected.

The evolution of redox/pH profiles through the near-field is indicated schematically in Fig. 5. Even though the applicability of Eh as a global parameter in low-temperature groundwater systems is questionable (Lindberg and Runnells, 1984), it is probably reasonable to consider solid phase buffering by iron minerals in all anaerobic conditions. The Eh is thus pH dependent and can be considered to lie between

$\text{Eh} = 800 - 59 \text{ pH (mV)}$  for equilibration with air and

$\text{Eh} = 0 - 59 \text{ pH}$  for control by the iron/magnetite couple or by  $\text{H}_2$  at a pressure of 1 atmosphere.

Relevant redox buffering reactions were discussed in more detail by McKinley, 1985.

The pH profiles in Fig. 5 consider the 2 extreme scenarios of negligible acidification and major acidification at the tunnel wall due to pyrite oxidation (cf. Chapter 3). By the time of canister failure ( $>10^3$  years), little difference in the Eh/pH profiles generated by these scenarios would be expected although some chemical differences may persist (e.g. in  $\text{SO}_4^{2-}$  concentrations).

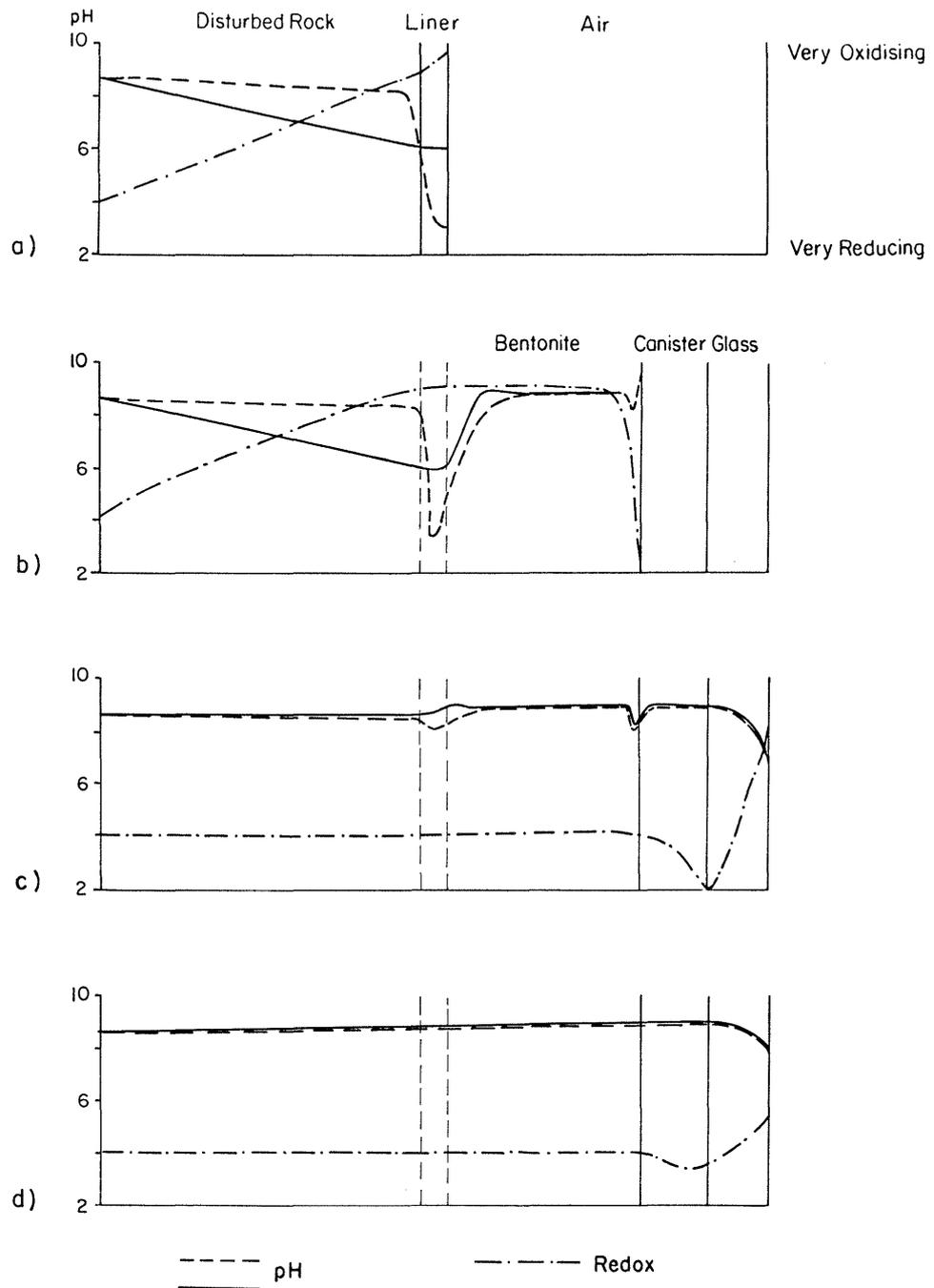


Fig. 5: Diagrammatic representation of pH/redox profiles through the near-field.  
 (Eh is a function of pH; with  $Eh = E^\circ - 59 \text{ pH (mV)}$ ). Very reducing conditions would correspond to  $E^\circ \approx 0$  while very oxidising conditions correspond to  $E^\circ \approx 800$ ).

a) during the operational phase  
 b) after  $\approx 10$  years  
 c) after  $\approx 10^3$  years  
 d) after  $\approx 10^5$  years

## 5 GLASS LEACHING AND NUCLIDE RELEASE RATES

### 5.1 Glass leaching

As the chemistry of the solution expected to contact the glass waste matrix in the sediment case is very similar to that considered in PG'85, due to buffering by the bentonite and canister corrosion products, there is no reason to expect any change in glass degradation rate. The discussion in McKinley (1985) should thus also be valid for this case. Equally, assuming a similar thermal and mechanical (handling) history, the PG'85 fracturing data and surface area for leaching should also be directly applicable.

More recent experimental work within the JSS project (JSS, 1988) has shown that, even at  $\approx 90^\circ\text{C}$ , long term degradation rates are compatible with the  $10^{-7} \text{ g cm}^{-2} \text{ d}^{-1}$  value in PG'85. Analogue studies suggest rates could be much lower (Jercinovic and Ewing, 1988), although such data for basaltic glasses should be treated with caution (Chapman et al., 1984). The JSS work also suggests that previous concerns about increased glass dissolution in the presence of bentonite are not justified at appropriate temperatures (supported by the work of Noguez et al., 1985). Some observed increase in the leaching rate in the presence of finely divided magnetite may not be relevant to the expected conditions, but, in any case, a value of  $2.5 \times 10^{-7} \text{ g cm}^{-2} \text{ d}^{-1}$  is taken to be conservative (Grambow et al., 1987). Although a higher glass corrosion rate is chosen, the GLASSOL model predicts glass lifetimes at  $90^\circ\text{C}$  of  $\approx 10^5$  years, similar to those derived in PG'85 (Grambow et al., 1987; JSS, 1988). At a more realistic temperature of  $50^\circ\text{C}$ , a glass duration of  $\approx 10^6$  years is predicted. Such an extended life is reasonable given the near-field Eh/pH conditions which would fall in a region in which "passivation and/or immunity" is expected (Jantzen, 1987).

### 5.2 Radionuclide release rates from the glass

Over long time periods, the degradation of the glass matrix can be considered to be congruent, but the release of individual radionuclides can be further constrained by their solubility in the leaching solution. Given the chemical buffering of the near-field, the elemental solubilities derived for PG'85 (McKinley, 1985) should also be applicable to the sediment study (Table 5). Note that these are elemental solubility limits and correspond to the sum over all isotopes of a particular element present (cf. Hartley, 1985).

It is likely that many of the values in Table 5 are very conservative. This is particularly the case for Pd and Sn which more recent calculations suggest to be totally insoluble in such reducing, slightly alkaline solutions. The far-field solubilities actually calculated (Wittwer & McKinley, 1989) are  $\leq 10^{-20} \text{ M}$  and, although

this absolute value is chemically meaningless, it indicates that dissolved species of these elements will be totally negligible. One exception to the general conservatism of near-field solubilities relative to far-field values is Se, calculations indicating somewhat higher solubilities than those used in PG'85 (McKinley, 1985). The lower value may, in fact, still be reasonable given the sulphide minerals in the system, as it is expected that mixed sulphides/ selenides would form before selenide concentrations were high enough to form pure mineral phases. Nevertheless, a solubility of  $10^{-7}$  M is probably preferable to ensure conservatism. Uncertainties in the Se and Pd databases are discussed further by Baeyens and McKinley (1989).

The Se case illustrates the general problem of gaps in the thermodynamic database used for solubility prediction. Missing solution species can lead to non-conservative under-prediction of solubility while missing solid phases lead to over-prediction. For such trace species, solubility is likely to be limited by solid solution in secondary minerals - for which no data are currently available.

In PG'85, near-field transport calculations (cf. Chapter 6) were used only as a basis for nuclide selection and not to define the source term for far-field transport. The far-field source term was evaluated with the code DREG (Hartley, 1985). This code modelled the fractured glass as equivalent spheres with congruent dissolution of all radionuclides. Release was further constrained by elemental solubility limits but, due to the uncertainties in defining near-field chemistry, solubilities applicable to the far-field were used in these calculations. Equivalent calculations for the sediment study, however, used the near-field solubility limits given in Table 5 which are not only logically more reasonable but also ensure that the source term is identical for both the OPA and USM.

**Table 5:** Solubility limits for the near and far-field

Element	log solubility (M)		
	Near-field (McKinley, 1985)	OPA (Wittwer and McKinley, 1989)	Far-field USM
Ac	-2		
Am	-2	-5	-3
Be	-4		
Cs	high		
Ca	-2	≈-4	≈-3
C	high	≈-2	≈-3
Cm	-2		
Ho	-8		
I	high		
Pb	-6		
Mo	-2		
Np	-8	-11	-12
Ni	-4		
Nb	-8		
Pd	-8 <sup>+</sup>	<-12	<-12
Pu	-6.5	-5	-5
Pa	-5.5		
Ra	-8		
Rn	high		
Sm	-8		
Se	-8 <sup>*</sup>	-7	-7
Ag	-4		
Sr	-4		
Tc	-7.5	-8	-8
Th	-5.5	-2	-2
Sn	-9 <sup>+</sup>	<-12	<-12
U	-9	-8	-10
Zr	-9		

\* -7 is probably now preferable - cf. text.

+ data probably extremely conservative, expected to be totally insoluble.

### 5.3 Sensitivity of nuclide releases to model assumptions

Assuming a congruent glass dissolution rate of  $10^{-7}$  g/cm<sup>2</sup>/day and an effective area of 21.4 m<sup>2</sup>, a glass dissolution time of  $5 \times 10^4$  years is calculated (McKinley, 1985) which is about a factor of 3 less than a more geometrically realistic model considering the fractured glass block as equivalent spheres (Hartley, 1985). From the nuclide inventories (Appendix 1), the release rates of individual nuclides can be readily calculated. Tables 6 and 7 list such release rates at a time  $10^3$  years after emplacement - equivalent to the earliest expected canister failure time. Assuming a more realistic canister life of  $\approx 8000$  years (cf. Chapter 4) would have little effect on these release rates beyond allowing a few short-lived nuclides to decay into insignificance (Ni-63, Sr-90, Ag-108m, Sn-121m, Cs-137 and Sm-151).

As noted in 5.1 above, modelling with GLASSOL suggests that a more realistic effective dissolution rate may be an order of magnitude below that assumed in PG'85. This would also decrease congruent nuclide release rates from the matrix by an order of magnitude. If a fairly arbitrary minimum significant release cut-off of 1 Bq/year/canister is considered, such a decrease would also allow Be-10, Sr-90, Sn-121m and Sm-147 to be excluded from further consideration.

An important further constraint on nuclide release rates is set by elemental solubilities. Although transport to the far-field occurs predominantly by diffusion (cf. Chapter 6), the magnitude of the solubility limitation effect can be seen by considering the entire advective flux to be focused through the near-field and allowing the nuclides to reach saturation. The results of such calculation for the 0.4 l/canister/year OPA base case are also presented in Tables 6 and 7. Equivalent values for the USM would be one order of magnitude higher. Although such a calculation is very pessimistic, it is clear that solubility would effectively limit releases in many cases - the controlling process is that yielding the smaller release rate which is underlined in the Tables. Applying the 1 Bq/year/canister release cut-off, Sn-121m and Sm-147 can be clearly excluded from further consideration for both the OPA and USM cases.

Inspection of Tables 6 and 7 also gives some indication of cases where the solubility limits - which are generally more uncertain than the glass matrix degradation rate - play a critical rôle. For example, although the Am and Cm solubilities chosen are probably over-conservative, values 3-5 orders of magnitude lower would have to be justified before solubility would be more important than leach rate.

The Pu, Np and U solubilities give performance "gains" relative to a simple congruent dissolution model of 2, 4 and almost 6 orders of magnitude respectively. The U value can, moreover, be defended by the fact that natural groundwaters tend, in any case, to be saturated in U and hence no significant increase due to the presence of

the repository is to be expected. For the fission/activation products, solubility is an important constraint for Se, Zr, Tc, Pd, Sn and Sm.

Although it may be possible to justify reducing the solubility assumed for some of these elements based on laboratory studies, greatest uncertainties are probably associated with Sn and Pd. These elements may, in fact, be totally insoluble under repository conditions and, if this can be demonstrated, need not be considered further in the safety analysis.

Table 6: Actinide release rates (per canister, 1000 years after emplacement)

Nuclide	$t_{1/2}$ (y)	Release rate limited by congruent dissolution		Solubility limited release rate (OPA)	
		(mol/y)	(Bq/y)	(mol/y)	(Bq/y)
Cm-245	8.5E3	7E-8	1E5	4E-3	6E9
Am-241	4.3E2	5E-6	2E8	2E-3	5E10
Np-237	2.1E6	7E-5	4E5	4E-9	2E1
U-233	1.6E5	2E-8	2E3	5E-14	4E-3
Th-229	7.3E3	4E-11	7E1	5E-8	8E4
Cm-246	4.7E3	7E-9	2E4	4E-4	1E9
Pu-242	3.8E5	4E-7	2E4	5E-9	2E2
U-238	4.5E9	2E-4	5E2	4E-10	1E-3
U-234	2.4E5	3E-7	1E4	6E-13	3E-2
Th-230	7.5E4	1E-9	2E2	1E-6	2E5
Ra-226	1.6E3	5E-12	4E1	4E-9	3E4
Am-243	7.4E3	7E-6	1E7	2E-3	4E9
Pu-239	2.4E4	6E-6	3E6	7E-8	4E4
U-235	7.0E8	3E-6	5E1	7E-12	1E-4
Pa-231	3.3E4	4E-11	2E1	1E-6	5E5
Pu-240	6.5E3	4E-6	8E6	5E-8	9E4
U-236	2.3E7	2E-6	9E2	4E-12	2E-3
Th-232	1.4E10	1E-10	1E-4	1E-7	1E-6

Table 7: Fission/activation product release rates (per canister, 1000 years after emplacement)

Nuclide	$t_{1/2}$ (y)	Release rate limited by congruent dissolution		Solubility limited release rate (OPA)	
		(mol/y)	(Bq/y)	(mol/y)	(Bq/y)
Be-10	1.6E6	5E-10	4E0	4E-5	3E5
C-14	5.7E3	4E-10	9E2	high	-
Ca-41	1.3E5	2E-9	2E2	4E-3	4E8
Ni-59	8.0E4	2E-7	4E4	4E-5	7E6
Ni-63	1.0E2	4E-11	5E3	7E-9	9E5
*Se-79	6.5E4	2E-6	4E5	4E-8	8E4
Sr-90	29	1E-14	6E0	4E-5	2E10
Zr-93	1.5E6	2E-4	2E6	4E-10	4E0
Nb-94	2.0E4	8E-9	5E3	4E-9	3E3
Mo-93	3.5E3	1E-10	5E2	4E-3	2E10
Tc-99	2.1E5	2E-4	1E7	1E-8	8E2
Pd-107	6.5E6	5E-5	1E5	4E-9	8E0
Ag-108m	1.3E2	6E-13	6E1	4E-5	4E9
Sn-121m	50	8E-16	2E-1	5E-20	1E-5
Sn-126	1.0E5	7E-6	9E5	4E-10	5E1
I-129	1.6E7	4E-8	3E1	high	-
Cs-135	2.3E6	6E-5	4E5	high	-
Cs-137	30	4E-13	2E2	high	-
Sm-147	1.1E11	3E-5	4E0	4E-9	5E-4
Sm-151	93	1E-9	2E5	2E-13	3E1
Ho-166m	1.2E3	1E-10	1E3	4E-9	4E4

\* using a conservative solubility of  $10^{-7}M$

## 6 RADIONUCLIDE TRANSPORT THROUGH THE NEAR-FIELD AND RELEASE TO THE GEOSPHERE

### 6.1 Transport through the bentonite

When the canister fails mechanically after  $\geq 10^3$  years, radionuclides leached from the glass will begin to be transported through the near-field towards the undisturbed far-field. The bentonite backfill plays two important rôles - its low hydraulic conductivity ensures that solute transport occurs predominantly by diffusion while its pore structure is assumed to preclude colloid transport. The latter assumption is critical to the applicability of solubility limits as constraints on nuclide release and, although not yet unambiguously proven, it is supported by the structural studies performed in the Buffer Mass Test at Stripa (Pusch, 1985). Even though large pores may be opened up in the event of gas flow through the bentonite (Pusch et al., 1985), they should be closed by the swelling pressure of the bentonite when gas pressures drop. The most reasonable model of the pore structure of compacted bentonite thus involves a connected network of pores with an average diameter of  $<$  approx. 100 nm with a number of unconnected macropores with average diameters approx. 0.25  $\mu\text{m}$  (Pusch and Karnland, 1986). The constrictivity and tortuosity of the pores narrows the effective throat size considerably but a minimum effective diameter of  $\approx 10$  nm may be more representative than the 2 nm average clay particle spacing (McKinley, 1985). Such a model agrees with the very low diffusivities ( $\approx 10^{-15}$   $\text{m}^2/\text{s}$ ) measured for macromolecules in such material (Grauer, 1986). For safety analysis purposes, colloids can be regarded as having effective diameters  $\geq 10$  nm (cf. Appendix III) and hence would be immobile in bentonite. Although there is very limited experimental work on colloid transport in bentonite at relevant compaction levels, that available supports the assumption that bentonite acts as an efficient colloid filter (cf. Appendix II of McKinley, 1985). Additionally, studies of the Boom Clay indicate very low mobility of organic molecules with effective diameter  $\geq 3$  nm (P. Henrion, pers.comm.).

Solute transport through highly compacted bentonite is extremely complex and there is currently no consensus on how best to model it. The simplest approach considers Fickian diffusion and fast, reversible, concentration-independent sorption ( $K_d$  model). This approach must be used with caution in any natural system (cf. McKinley and Hadermann, 1984) and is particularly questionable for bentonite if sorption data from batch experiments are extrapolated to a highly compacted system. Although sorption on finely divided clays is generally fast, it is often partially irreversible and concentration dependent (McKinley and Hadermann, 1984; Anderson and Chiao, 1985; Grauer 1986). Even taking such perturbations into account, however, it is clear that the relative "diffusivities" measured for various radionuclides are not related to relative sorption (Torstenfelt et al., 1983). A number of different models have been postulated to explain such discrepancies.

In the surface diffusion model (Neretnieks, 1982; Charles et al., 1986; Muurinen et al., 1986; 1987) it is considered that diffusion occurs in both the pores and in the sorbed phase. The model is somewhat strange in that the general expectancy is that the movement of strongly sorbed species on a surface would be slow at  $\approx 25^\circ\text{C}$  relative to diffusion in solution. In addition, this model seems only to hold for specific nuclides - explicitly inapplicable to most actinides (Neretnieks, 1982) and Co (Muurinen et al., 1986). A further general problem with the model is that, in calculating the diffusion in the porewater, it assumed the "available" porosity is the same for all nuclides. As bentonite is microporous with predominantly negatively charged surfaces (at expected pH values), it is to be expected that the available porosity will depend strongly on both nuclide size (of the aqueous complex) and charge. The importance of this factor is clearly evident from the fact that, not only do measured diffusivities vary considerably with the extent of compaction, but the relative diffusivities of charged species and labelled water also change (cf. Grauer, 1986; Relyea et al., 1986).

The double-diffusivity model developed by Cheung (1988a, b) goes some way towards considering the macro-porosity (available to anions) and micro-porosity (available to cations only) separately. This model has, to date, only been applied to  $\text{Cs}^+$ ,  $\text{I}^-$  and  $\text{Cl}^-$  and, even then, assumes no Cs sorption - which is known to be unrealistic.

Torstenfelt (1986a, b) does not explicitly partition porosity, but assigns a number of "diffusivities" (up to 3), to individual nuclides. Although discussed in terms of preferential transport paths, this approach is basically empirical and cannot distinguish between different flow mechanisms and variable speciation of the nuclide involved. This latter point is particularly important for redox sensitive nuclides when various additives are included in the bentonite (e.g. powdered Fe, pyrite, etc.) to ensure reducing conditions. Neither the efficiency of such redox buffers nor possible complications due to their sorption properties have been fully evaluated.

Probably the most satisfactory model of transport through compacted bentonite is that based on the microstructural studies of Pusch and co-workers (Pusch and Hökmark, 1988). This model predicts that the proportion of the total porosity available to anions will vary with the degree of compaction. At a saturation density of  $2.1 \text{ Mg/m}^3$ , only 5% of the total porosity (34%) would thus be available. In such a system it is reasonable to select a small dissolved gas molecule (e.g. He,  $\text{N}_2$ ) as a non-interacting tracer. Unfortunately, the closest data found were for  $\text{H}_2$  and  $\text{CH}_4$  which may, in the case of oxidised clay, interact to some extent (P. Henrion, pers. comm.). Nevertheless, data for  $\text{H}_2$  were selected which, in compacted bentonite, has a diffusivity ( $D_a$ ) of  $\approx 10^{-11} \text{ m}^2/\text{s}$ . Even without further retardation, therefore, anions (inorganic C, I, Mo, Pd, Se and Sn) would have diffusivities  $\approx 5 \times 10^{-13} \text{ m}^2/\text{s}$ . Although cations

would have access to all of the pore space, with increasing compaction more of this will tend to be interlamellar - access to which may be kinetically slow. The "available" surface per unit volume (or mass) thus decreases with compaction and hence batch sorption data would need to be scaled down. Taking the conservative sorption data from Table 8, the retardation resulting from sorption processes decreases diffusivity by  $\approx 1$  order of magnitude for Sr and Cs (to  $\approx 10^{-12}$  m<sup>2</sup>/s) and 2-3 orders of magnitude for the actinides ( $10^{-13}$ - $10^{-14}$  m<sup>2</sup>/s).

Table 8: Sorption data for bentonite backfill (McKinley and Hadermann, 1984)

Element	$K_d$ (m <sup>3</sup> /kg)	
	Realistic	Conservative
Ac	5	1
Am	5	1
Be	0.01	0
Cs	0.2	0.02
Ca	0.2	0.02
C	0.005	0
Cm	5	1
Ho	2.5	0.25
I	0.005	0.001
Pb	1	0.001
Mo	0.005	0.001
Np	1	0.1
Ni	1	0.05
Nb	2.5	0.02
Pd	0.005	0.001
Pu	5	1
Pa	1	0.1
Ra	0.2	0.02
Rn	0	0
Sm	2.5	0.25
Se	0.005	0.001
Ag	0.5	0.01
Sr	0.2	0.02
Tc	0.25	0.01
Th	1	0.1
Sn	0.05	0.001
U	1	0.1
Zr	5	0.25

It is clear from the discussion above, however, that considerable uncertainty exists in the modelling of long term transport through highly compacted bentonite. More experimental data are required in order to resolve the questions involved - in particular examining transport over larger scales to minimise experimental problems (migration times >1 year), attempting redox control without incorporation of solid additives (which are potential sorbants) and examining competition effects of the type to be expected in the near-field (e.g. McKinley and West, 1987).

## 6.2 Release into the far-field

The profiles of radionuclide release at the bentonite/sediment interface are dependent not only on the nuclide diffusivities through the bentonite but also on the details of near-field hydrology. In a simple case, it can be assumed that the entire flux past each canister flows through the disturbed zone at the tunnel wall where it can be represented by a mixing tank. The inner boundary conditions for such calculations is either a constant release rate (for matrix release limited nuclides) or a constant concentration (for solubility limited nuclides). The simple  $K_d$  model can be used to evaluate retardation and radioactive decay and ingrowth can be readily taken into account (Hopkirk et al., 1986). The results from such calculations in PG'85 (e.g. Fig. 6) were used to select radionuclides for consideration in the far-field transport models using a fairly arbitrary "insignificant release rate" cut-off criterion. In this case, any nuclide released into the far-field at rates of <1  $\mu\text{Ci}/\text{canister}/\text{year}$  was considered to be negligible and excluded from further consideration. As mentioned in Chapter 5, release rates for all other nuclides used in the far-field transport calculations do not take retardation by the bentonite into account.

If the basic transport model used is accepted, the effects of the differences between the sediment near-field and that in PG'85 can be discussed qualitatively with regard to key element selection:

- a) **Geometry:** The smaller tunnel radius in the sediment case would decrease transit times through the bentonite, thus increasing the release rates of nuclides which decay significantly during transport. Based on the matrix release limits (cf. Appendix II), the only additional nuclides which could reasonably pass a 10 Bq/canister/year cut-off would be  $^{129}\text{I}$ ,  $^{14}\text{C}$ ,  $^{59}\text{Ni}$ ,  $^{41}\text{Ca}$  and  $^{93}\text{Mo}$ . If credit is taken for sorption within the disturbed zone itself, the geometry of the PG'85 calculations can be accepted directly.
- b) **Solubility limits:** Most recent data indicate that Pd and Sn are totally insoluble, and hence need not be considered further, but suggest Se may be more soluble which would, in the conservative case, directly increase release of this nuclide by an order of magnitude.

In summary, therefore, the key fission/activation products for far-field transport calculations would be  $^{79}\text{Se}$ ,  $^{135}\text{Cs}$  and  $^{99}\text{Tc}$ . The long-lived actinides, e.g.  $^{238}\text{U}$ ,  $^{237}\text{Np}$ , will inevitably break through the bentonite even if transit times are very long, bringing

their daughters in secular equilibrium. Some of the shorter-lived actinide parents would, however, decay into insignificance during transit (certainly all isotopes of Am and Cm and probably all isotopes of Pu).

So far only the simple mixing tank boundary condition has been considered but releases to the far-field would be further decreased by taking into account boundary resistance at the bentonite/disturbed sediment interface or heterogeneous flow (fissures, sand channels). The latter case, in particular if most advective transport occurs in a few distinct features (Hopkirk et al., 1986), can decrease releases by many orders of magnitude such that very few nuclides would penetrate into the far-field at significant concentrations for a realistic scenario (McKinley, 1985). The influence of near-field hydrology on release profiles is discussed further in Chapter 7.

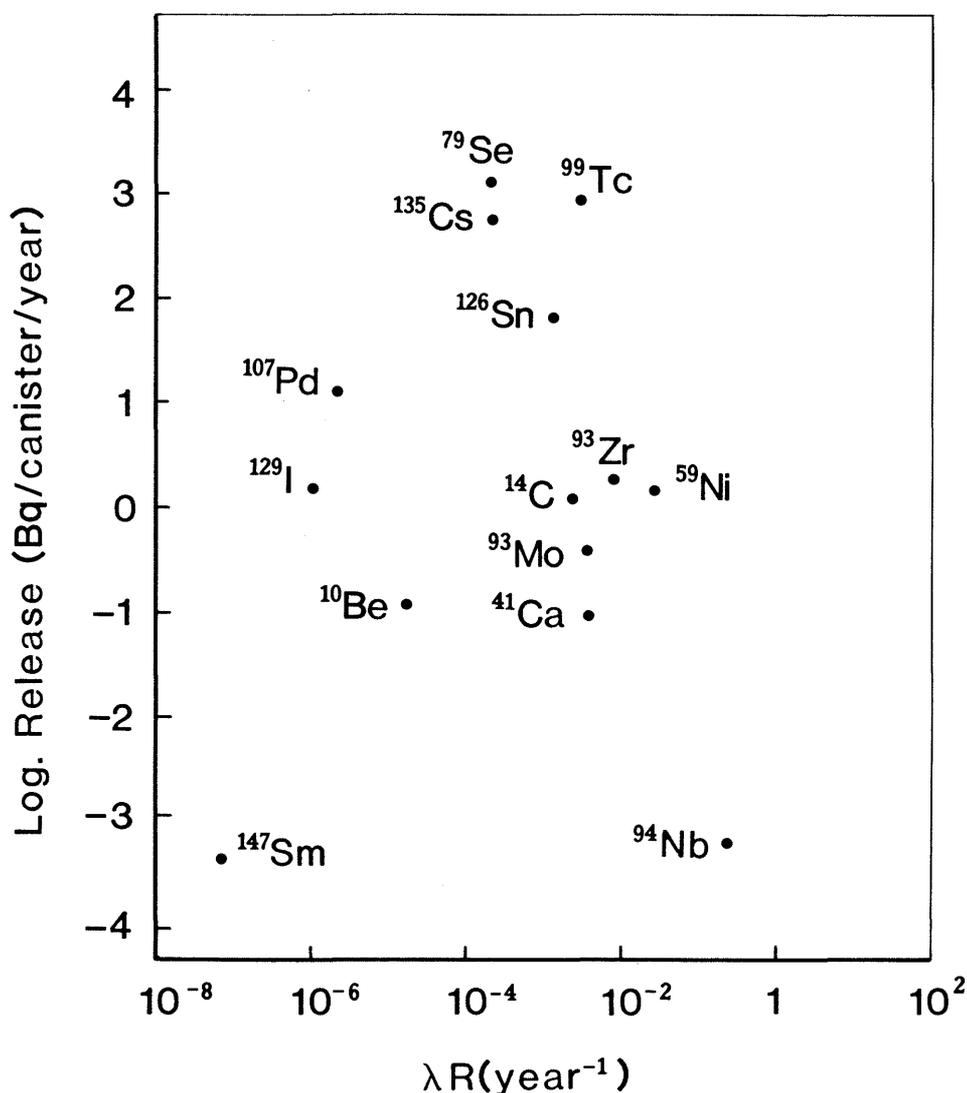


Fig. 6: Steady-state nuclide release fluxes to the PG'85 far-field calculated using a mixing tank boundary plotted against the product of the radioactive decay constant ( $\lambda$ ) and the retardation factor ( $R$ ) (from Nagra, 1985)

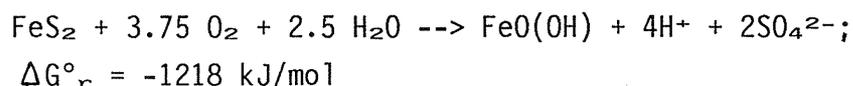
## 7 PROBLEM AREAS AND VARIATIONS ON THE BASE CASE

### 7.1 Microbiology

Analysis of the crystalline rock disposal option has indicated that some microbial activity could be expected in a deep HLW repository but the consequences of such activity would not significantly perturb the PG'85 safety case (McKinley et al., 1985). In this analysis, the major constraint on microbial activity was shown to be the rate of supply of chemical energy into the system, although the low availability of organic carbon could also be important. These conclusions are supported by studies of other conceptual HLW disposal systems in crystalline rock (West et al., 1984).

The situation for a sediment host-rock has not been analysed in detail, but microbiology cannot be so easily dismissed in this case. There is, indeed, evidence that microbially-catalysed processes were not only important during early diagenesis of the sediments (e.g. pyrite formation associated with sulphate reducing bacteria) but are also geochemically significant at the present time (e.g. producing methane in-situ - Wittwer and McKinley, 1989) and significantly altering natural hydrocarbon profiles in upper layers of the OPA (Schaefer and Leythaeuser, 1984). Additionally, the oxidation processes anticipated in the disturbed sediment zone (cf. Section 3.1) correspond to a considerable source of energy which could be utilised by microbes in conditions with relatively high contents of available organic carbon.

To evaluate the scope of the problem, the  $2.3 \times 10^4$  moles of pyrite considered to be oxidised around each canister in Section 3.1 can be expressed as



which, at pH=7, would correspond to a free energy change ( $\Delta G_r$ ) of -1378 kJ/mol. The total "available" free energy is thus approx.  $3 \times 10^7$  kJ around each canister, which is an order of magnitude greater than that calculated for the major energy source in the PG'85 repository - anaerobic corrosion of the waste canister (McKinley et al., 1985). Using the conversion factor of 64 kJ/g dry weight, this would be sufficient to produce an integrated organic biomass of approx.  $4.7 \times 10^5$  g (dry weight). An organic carbon concentration of the host-rock of 1 % corresponds to an organic carbon content of  $1.9 \times 10^6$  g in the disturbed zone, and hence such biomass production could be supported heterotrophically without recourse to energetically unfavourable autotrophic carbon fixation. The utilisation of such carbon (or at least, the lighter fractions of it) has been demonstrated in the upper layers of the OPA (Schaefer and Leythaeuser, 1984). An oxidising environment in the host rock occurs only during the very early stages of repository life, and any mobile organics produced may be assumed to have dispersed in the period of more than one thousand years before earliest nuclide release from the bentonite.

Previous safety analyses have shown clearly that the most important potential perturbation of the base case due to microbial activity arises from the effects of metabolic byproducts (McKinley et al., 1985; Grogan, 1987). Inorganic by-products, such as sulphuric acid, have been discussed previously (Section 3.1). The effects of organic metabolites will be considered in Section 7.3.

Direct effects due to the presence of microbial activity outside the bentonite would include radionuclide uptake onto/into microbial cells. Generally, such uptake would be expected to immobilise radionuclides although, in some cases, the cells may be mobile - in effect organic colloids (cf. next section). Microbial movement (taxis) can proceed against hydraulic gradients or through microporous environments. A requirement for such taxis, however, is the presence of a driving gradient in the concentration of a nutrient or energy source and, outside the bentonite, such gradients would be expected to be very localised and would not result in large-scale transport.

As the area within the bentonite is very little affected by the host-rock, the previous analysis for that region (McKinley et al., 1985) should still be applicable, as would be the general conclusion that the effects of microbial perturbations are within the margin of conservatism of the basic safety analysis which does not include these processes. Indeed with the increasing focus on Se as a key nuclide (cf. Section 6.2), microbial catalysis of the reduction of any selenate or selenite which may be leached from the waste glass (due to local radiolytic effects) by sulphate-reducing bacteria might usefully complement slow redox equilibration with canister corrosion products.

## 7.2 Colloids

A brief overview of natural colloids and their particular significance in a safety assessment context is presented in Appendix III. The colloidal size range includes inorganic complexes and polymers, clay minerals, organic complexes and microorganisms. In real life, the effects of these various components are difficult to separate. For the sake of simplicity, however, only inorganic species are considered here; microorganisms have been discussed in the previous section and organic complexants are examined in the following section.

Three sources of such inorganic colloids can be identified in the near-field:

- a) Supply in groundwater
- b) Erosion of engineered barriers (particularly bentonite)
- c) Precipitation of newly formed phases.

As yet, no data are available on the concentration of natural colloids in the reference sediment groundwaters. Data from dispersion of Boom Clay (Henrion et al., 1985) suggest that most of the colloidal size material in the clay is organic in nature but it is noted here that, above an operational cut-off of  $0.2 \mu\text{m}$  (not settled by 3 hours at  $2.3 \times 10^3 \text{ G}$  centrifugation), it seemed to be predominantly alumino silicates. Klenze and Kim (1986) measured colloid concentrations from  $10^9$  -  $10^{12}$  particles per litre in a range of groundwaters but the samples were pre-filtered to only  $<0.45 \mu\text{m}$  and the technique used does not distinguish between organic and inorganic species. Degueldre et al. (1987) measured at the FLG approx.  $10^{10}$  particles/l in the size range of  $0.1$  -  $1 \mu\text{m}$  which had a significant silica content (associated with organic carbon). Although in a granitic rock environment, the water conducting zones at the FLG are infilled with argillaceous material and hence, in the absence of further data, this latter concentration can be used for scoping calculations for a fractured clay or one containing conductive discontinuities. For spheres of a diameter of  $0.5 \mu\text{m}$ , such a concentration would correspond to approx.  $1.7 \text{ mg/l}$  which, if it was predominantly silica, would correspond to approx. 10 % of the concentration of dissolved silica (in either FLG or sediment water).

As far as the second source of colloids is concerned, the work at Stripa has shown no measurable erosion during the buffer mass test (Pusch, 1985). This has been interpreted as implying that no significant erosion would occur as long as advective water flow occurs in fissures with apertures of less than about a few millimetres. Although the buffer test concentrated on perturbation of the buffer rather than sources of colloids to the far-field, the evidence available suggests this source of colloids might be unimportant in the OPA. The potential erosion due to a large sand channel in the USM cannot be evaluated at present but could, potentially, be large.

The third source of colloids, arising from direct precipitation, is very difficult to evaluate quantitatively as, by definition, such particles are thermodynamically unstable and owe their existence to kinetic factors, for which very little data exist. The main sources of such colloids would, however, be regions of active corrosion (canister or glass surfaces) or regions of chemical gradients (particularly in Eh or pH). After the perturbation from the operational phase has diminished, most of the corrosion reactions and chemical gradients will exist within the bentonite (cf. Fig. 5) and hence their overall significance will be small assuming no colloid transport occurs through the compacted backfill (cf. Section 6.1).

As far as near-field analysis is concerned, therefore, the main concern is with the behaviour of colloids in the disturbed host rock around the emplacement tunnels. Colloids formed within the bentonite will be effectively immobile (cf. Section 6.1) and any influence they would have on repository performance would tend to decrease the rate of radionuclide release from the near-field and hence can be conservatively ignored.

Colloid transport within the disturbed zone will be dependent on:

- a) the natural flow system (micro scale)
- b) the effects of mechanical disturbance
- c) groundwater chemistry and the effects of oxidation/subsequent re-equilibration with reducing waters.

At present, there are insufficient data to quantitatively evaluate the net consequences of these three processes. Qualitatively, however, it could be considered that mechanical creep and formation of secondary minerals could well seal microporous structures in disturbed clay, but there is no conceivable mechanism which could be expected to seal major sand channels in the USM.

The most important effects of colloids formed or naturally present outside the bentonite are those which enhance transport of radio-nuclides. In the simplest case, if nuclides precipitate at a pH front or are sorbed onto colloidal material, their concentration at the outside of the bentonite is decreased which thus enhances the rate of diffusion through this barrier (i.e. in the worst case this results in a zero concentration external boundary condition rather than mixing tank in which concentrations build up in the low water flux past the near-field). Much more importantly, such colloidal species might be transported through the disturbed zone with minimal retardation. As long as the net water flux is roughly perpendicular to the tunnel orientation, the significance of such transport would not be large (although it could be significant as a mechanism of transport to sand channels in the USM) but with flow roughly parallel to the tunnels it could be important. Colloid transport models, which take into account retardation processes (filtration, sorption), aggregation/disaggregation and solute interaction, are under development but, as yet, are at a fairly early stage. In addition, it is assumed that the "disturbed zone" properties persist until the period when radionuclides are released from the bentonite which is  $>10^3$  years after closure (and probably  $>10^4$  years for most relevant nuclides) which may be unduly pessimistic. More work in this field is required, however, before this process can be treated in a more qualitative manner.

### 7.3 Natural organics

Both OPA and USM, contain significant concentrations of organic carbon ( $\approx 1$  % by weight), which exists predominantly as large molecular weight humic acids (Wittwer and McKinley, 1989). The persistence of such material indicates its low mobility which is compatible with experimental data from the Boom Clay (Henrion et al., 1985). As far as near-field performance is concerned, the main concern is the low concentration of small molecular weight species which may be mobile and penetrate the bentonite. The larger size species, even if mobile, behave like inorganic colloids and hence the discussion in the previous section can be considered directly applicable. The relevance of such dissolved humic acids to far-field transport is discussed by Wittwer and McKinley (1989).

For the expected pore structure in bentonite (cf. Section 6.1), mobile molecules would have sizes  $<10$  nm (effective diameter) which corresponds to molecular weights  $\approx 10^4$  daltons. This size would, however, apply only to uncharged species, whereas most of the humic acids would be dissociated to a considerable extent at the neutral/alkaline pH of the porewater. Charge repulsion between negatively charged humic acids and clay surfaces would further decrease the effective pore size. At present it is not possible to rigorously specify a cut-off size for organic penetration of bentonite, but a molecular weight of a few thousand amu would seem to be about the correct order of magnitude. Laboratory experiments show a distinct decrease in diffusivity with increasing size. The diffusivities for sizes  $\approx 250-10^3$  daltons are  $\approx 10^{-15}$  m<sup>2</sup>/sec which, for a simple 1D, constant source, diffusion calculation corresponds to penetration of a 10 % concentration front through the 80 cm bentonite annulus in  $>10^6$  years (e.g. Duursma and Eisma, 1973). Such transport rates can be considered negligible.

The conclusion above does not, however, hold for smaller organic molecules, especially if they are less highly charged. Data from the OPA (Schaefer and Leythaeuser, 1984) suggests that these are present only at very low concentrations - (C<sub>2</sub>-C<sub>7</sub>) hydrocarbons, for example, correspond to only  $\approx 0.01$  % of the total organic carbon in the rock. Such low concentrations ( $\approx$ ppb), especially in the light of the lesser complexing ability of these species relative to chelating humics and the much higher concentrations of inorganic ligands (e.g. OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>) would imply that perturbation of near-field releases would, again, be small.

#### 7.4 The tunnel liner

In the previous discussion it has been assumed that an effectively inert steel liner is present during the operational phase which is withdrawn after waste emplacement. Such a system has the advantage of greatly simplifying the near-field analysis but may not be practicable. In this section we consider the possible influence that the liner would have if it was left in place.

It might be noted that, for optimisation of costs, a concrete liner might be preferred to steel. This would, however, greatly complicate the near-field analysis as neither the bentonite nor the clay minerals of the host rock are thermodynamically stable in contact with the highly alkaline concrete porewaters and might alter quite rapidly. Although it is quite possible that the overall performance of the near-field would still be acceptable in this case (e.g. zeolites, which can be formed from clays at high pH, have many favourable properties), too little data are currently available to justify examining this option in detail and hence it will not be considered further at this stage. The database required for such an analysis is, however, high on the priority list for L/ILW repository safety analysis and hence it may be possible to evaluate this option in the near future.

Basically, two different types of liner could be envisaged - one which was as impermeable as possible (thus reducing host rock oxidation, cf. Section 3.1) or one which was made deliberately permeable (e.g. due to perforations).

In the former case, water would not penetrate through the liner while the disturbed host rock was resaturating and thus the engineered barriers may remain dry during the early parts of the thermal transient. The lower thermal conductivity of the dry bentonite will increase peak temperatures within the bentonite annulus which may cause complications (cf. Section 3.3). The pressure build up round the liner due to creep of the rock will, eventually, cause mechanical failure of the liner which, due to the likely anisotropy of this creep and possible heterogeneity of corrosion, could well be quite localised. Such localised failure has been well documented for tunnels suffering from acid drainage (Rainey and Rosenbaum, 1989). Wetting of the bentonite will thus also be localised as will be the resulting pressure build-up due to consequent swelling. At early stages of bentonite resaturation, therefore, complex pressure distributions could exist within the near-field which could cause early mechanical failure of the canister or even serious distortion of near-field geometry and displacement of the canister. As yet, no calculations have been performed to examine such failure modes quantitatively, but it is to be expected that they would be very complex and poorly supported by experimental data. In any case, it has been argued that wetting of the bentonite would be driven by capillary suction which would rapidly homogenise the system. Alternatively, engineered solutions to the problem of uneven wetting could be envisaged, such as designing the liner for specific failure modes.

An obvious alternative to the impermeable liner would be one with regular perforations, to ensure that wetting occurs evenly (assuming that the damaged zone around the tunnel is sufficiently conductive to even-out water supply outside the liner). Such a liner would, however, provide no barrier to oxidation of the host-rock. Various options could, however, be considered which combine the best of both extremes by filling such perforations with soluble or preferentially corroding materials which would open shortly after emplacement or, indeed, drilling perforations in the final stages of backfilling.

Although the structure of the liner would be quite complex in order to achieve the desired mechanical properties, from the geochemical point of view it can be regarded as a simple thin cylinder. The liner design and inventory of steel required is not yet specified in detail but, assuming a minimum thickness of 5 mm, this would correspond to 0.4 m<sup>3</sup> of Fe per canister. This corresponds to approx. 45 % of the mass of Fe in the canister and hence would have a significant impact on the overall geochemistry. In addition to providing a further redox buffer, the resulting Fe corrosion would act as a sink for oxidants and could somewhat extend the expected canister life although the factor involved would not be expected to be more than about 50 % (corresponding to removal of the sulphate

corrosion component to overall corrosion). In the case of a very acidic environment at the tunnel wall, corrosion of the liner could be very rapid but would consume protons and thus increase the pH.

The Fe oxyhydroxide corrosion products could also act as a large surface area sorbant which might significantly retard some of the poorly sorbing species (e.g. anions such as I<sup>-</sup> or Se<sup>2-</sup>) in the event that the lower available surface area of the canister corrosion products is not taken into account. On the negative side, Fe corrosion could produce colloidal particles which would have high sorption capacities and, as they are formed outside the bentonite, might be assumed to be mobile in the far field.

### 7.5 Variations in near-field hydrology

In principle, an increased flux of water through the repository will increase the rate of degradation of engineered barriers and hence the rate of release of solubility limited nuclides, but will have little influence on the release of matrix-release limited nuclides. In fact, due to the diffusional resistance of the bentonite, the increases will not be directly proportional to the flow rate (cf. discussion in NGB 85-04, pp. 6-47 to 6-49). In addition, releases of some key nuclides would quickly transfer from solubility- to leach-controlled. The assumed Se solubility, for example, lies only one order of magnitude below the matrix release limit (cf. Table 3, Appendix IIa) and hence the maximum increase in Se release would be constrained to this factor. An increase of 2 orders of magnitude in total flux would thus increase the total flux of fission products by approx. 1 order of magnitude with the relative contributions by Cs and Tc increased relative to Se.

The simple assumption of a homogeneous flux through the repository, all of which can exchange solute with the near-field (cf. Section 2.2) is obviously a great oversimplification.

The importance of assessing the distribution of flow in the homogeneous case was mentioned in Section 6.2 when the calculations by Hopkirk et al. (1986) showing the possibility of great decreases in release rate were considered. The disturbed zone around the tunnel could provide an important flow path, possibly connected to adjacent aquifers via the disturbed zone around the shaft. For the sediment case this could, potentially, be much more serious than the crystalline case because of the more extensive chemical alteration possible in sediments and the much higher hydraulic gradients which could be expected. There is, at present, no way of rigorously assessing the relative importance of such a flow path but, given that sources of colloidal material are present in this zone (Section 7.2), it needs to be evaluated on both a regional and microscopic scale.

The reference water flux through the formations considered has a large associated uncertainty arising both from the boundary conditions set by the regional hydraulic model and the large scale hydraulic properties assumed (Nagra, 1988). The values selected are, however, probably a reasonable basis for scoping calculations and may well be quite conservative.

## 8 OVERVIEW AND CONCLUSIONS

### 8.1 Overview of performance - evidence from natural analogues

The overview presented in this report can only be considered as semi-quantitative as it involves considerable interpolation, synthesis and interpretation of data from diverse sources and extrapolation of data from laboratory and field timescales to the geological scales involved in safety assessment. In individual cases, evidence from natural systems (natural analogues - cf. Chapman et al., 1984) is used to help justify such extrapolations. Natural analogues can also, however, be used in a less quantitative sense to assess the overall conclusions of the safety analysis in a more general way, i.e. is there evidence for the persistence of thermodynamically unstable, geochemical anomalies in such formations for geological periods of time?

On a micro scale, the observed redox halos in Permian sediments (Hofmann et al., 1988; Hofmann, 1989) show clear evidence of immobilisation of a large number of elements (including Ni, Se, Pd, Pb and U) due to local redox conditions. High concentrations of these elements have persisted for tens of millions of years and, although there is some evidence of recent remobilisation (within the last  $10^6$  years), this is evidently a very slow process and illustrates the great potential of bulk clays for radionuclide immobilisation. In this particular case, microbial catalysis of redox reactions may be the driving force for the concentration and immobilisation of these trace species.

The presence of organic materials has been repeatedly mentioned as a potential problem, but evidence from recent sediments has indicated that such organics can immobilise elements of such disparate chemistry as I (Loch Lomond site, Hooker et al., 1985) and U (Needles Eye site, Hooker et al., 1986).

The evidence above, however, applies only to homogeneous clay bodies. Of particular interest is the effect of heterogeneities - fractures and sand channels. Evidence of preferential mobility in and around fissures in the OPA exists only in surface exposures where penetration of oxidation fronts along such features is obvious. It is not clear if these fissures would also provide preferential flow paths at repository depths. The USM, however, shows evidence of local oxidation even at depth, although such oxidation may have occurred at an early stage of diagenesis. Particularly noticeable, however, is the loss of organics and the transformation of pyrite to iron oxyhydroxides associated with the oxidation (Wittwer and McKinley, 1989) implying more facile movement of the organics than was the case for OPA (Schaefer and Leythaeuser, 1984).

A planned study of natural series radionuclide mobilisation from the vicinity of fissures in OPA, similar to those carried out in crystalline rock (Alexander et al., 1989) may yield more quantitative information on overall radionuclide mobility in the presence of high organic carbon concentrations.

## 8.2 Technical conclusions

The overall performance of the near-field for the sediment study base case is seen to be very little different to that predicted in PG'85. Engineered barrier lifetimes would be relatively unaffected by changing the host-rock and the predicted radionuclide release profile to the far-field is changed mainly by the use of near-field solubilities (rather than far-field as in PG'85). Although this change makes direct comparison with PG'85 more difficult, it is conceptually more correct and also simplifies comparison of OPA with USM. Taking into account data reported since 1984 changes the relative importance of some nuclides - emphasising Se and diminishing Sn and Pd. A more fundamental factor is the decrease in tunnel diameter relative to PG'85, which could increase the number of fission products to be considered in the far-field.

In terms of potential perturbations, the greatest effects could arise from oxidation of the host-rock during the operational phase. This could perturb water chemistry and near-field hydrology and serve as a source of colloids and organic complexants derived from microbial activity. In this regard, the presence of a corroding steel liner could also be significant. These sources of colloidal material **outside** the bentonite mean that the simple arguments used PG'85 no longer hold and effective far-field colloid retardation mechanisms must be invoked in order to justify a transport model including only dissolved radionuclide species. (This may, in any case, be required if significant colloidal concentrations are found in the natural groundwater.)

As in PG'85, the discussion of the main problem areas - microbes, colloids and organic complexants - is largely qualitative. Despite a considerable increase in effort in these areas, rate of progress towards rigorous, quantitative treatment has been slow due to practical constraints on the rate at which laboratory and field data can be accumulated and the theoretical problems involved in modelling systems which are kinetically rather than thermodynamically controlled. These problems may be more severe for sediments than the PG'85 crystalline.

## 8.3 Recommendations for future work

From the discussion in the previous chapters, it is clear that several areas are now fairly well characterised or are not very critical for the safety analysis and would have a low priority for future research - e.g. mineralogical stability of bentonite, canister corrosion rates, glass corrosion rates, radiolysis etc. Some areas can be highlighted, however, in which further work is in progress or in which new projects will be started:

- i) Evaluation of chemical profiles through the near-field. The sketches in Fig. 5 could be more rigorously established using a chemical equilibrium/transport code (e.g. CHEQMATE - Sharland et al., 1987). Prior to use of such a code, however, the various chemical reactions involved in the disturbed zone, bentonite, canister and glass (and at the interfaces) need to be carefully evaluated in order to establish the dominant processes over the timescales considered. Of particular interest is the formation and longevity of strong chemical gradients (especially of pH or Eh). Such gradients can act favourably as "chemical traps" for migrating solute but could be a location for detrimental colloid formation.
- ii) Quantification of diffusion of key nuclides (or solutes) through compacted bentonite. In the absence of a good mechanistic model, empirical diffusion experiments under realistic conditions must be used to allow better evaluation of the barrier rôle of bentonite. Achieving such "realistic" conditions is experimentally very difficult and a continuing investment of effort is justified.
- iii) Measurement of the solubility of some key elements. The near-field analysis would be simplified if some poorly characterised elements could be shown to be insoluble - e.g. Sn, Pd. If a lower solubility for Se could be demonstrated, this would have a direct input on this major contributor to dose.
- iv) Improved near-field heat-flow/resaturation calculations. Because of the reduced tunnel diameter relative to PG'85 and differences in sediment thermal properties, temperatures throughout the bentonite could exceed 100°C leading to possible loss of swelling capacity. Accordingly, it may be worthwhile to study this effect (Couture effect) further. Alternatively, the option of increased storage time prior to disposal should be evaluated.
- v) Bentonite rheological properties. The bentonite forms a major barrier, and it is important to be sure that excessive canister sinking will not occur. Further experimental and modelling studies, taking into account possible long-term changes in the physical characteristics of bentonite, could enhance our understanding. If necessary, sinking problems could be "engineered out" by the construction of support structures but, following the policy of keeping the near-field as simple as possible, it would be preferable to demonstrate conclusively that such efforts were not required.
- vi) The development of models to assess the influence of colloids, organics and microbes on near-field performance is an area which is being actively pursued.

- vii) Evaluation of the performance of various liner designs and optimisation with respect to repository performance. From the engineering side, concrete liners may offer advantages and the long-term stability of both bentonite and host rock in contact with such material should be evaluated.
- viii) The present study considers only vitrified HLW. For completeness, a similar analysis for other waste types which may also be included in such a repository (e.g. long-lived ILW) should be carried out.

As noted in the crystalline near-field study (McKinley, 1985), there are strong indications that the nuclide releases from the engineered barriers in a reasonable hydrogeological/geochemical environment would be of negligible radiological significance. The work noted above would provide a sounder scientific basis for incorporation of a more realistic near-field model in the safety analysis model chain.

Many of the studies suggested are generic (or involve generic components) and hence of direct relevance in many disposal programmes. The Nagra research programme should avoid duplication of work in progress elsewhere. It is strongly recommended that existing contacts with other national programmes should be continued and strengthened with the aim of maintaining an open forum for exchange of information about near-field models and databases. Such an enhanced background of information will ensure the continued relevance of priorities and milestones within the Nagra long-term near-field research programme.

## 9

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**Appendix I:** Inventories of radionuclides (per canister, 1,000 years after emplacement) from Nagra (1985)

Decay chain	Nuclide	Half-life (y)	Inventory (mol)	Nuclide	Half-life (y)	Inventory (mol)
1	Cm-245	8.5E3	3.5E-3	Be-10	1.6E6	2.6E-5
	Am-241	4.3E2	2.7E-1	C-14	5.7E3	1.9E-5
	Np-237	2.1E6	3.6	Ca-41	1.3E5	8.7E-5
	U-233	1.6E5	1.0E-3	Ni-59	8.0E4	1.1E-2
	Th-229	7.3E3	2.1E-6	Ni-63	1.0E2	1.8E-6
			Se-79	6.5E4	9.3E-2	
2	Cm-246	4.7E3	3.4E-4	Sr-90	29	6.1E-10
	Pu-242	3.8E5	2.3E-2	Zr-93	1.5E6	1.1E1
	U-238	4.5E9	8.0	Nb-94	2.0E4	3.9E-4
	U-234	2.4E5	1.3E-2	Mo-93	3.5E3	6.6E-6
	Th-230	7.5E4	4.9E-5	Tc-99	2.1E5	1.1E1
	Ra-226	1.6E3	2.4E-7	Pd-107	6.5E6	2.5
			Ag108m	1.3E2	2.8E-8	
3	Am-243	7.4E3	3.5E-1	Sn-121m	50	4.2E-11
	Pu-239	2.4E4	3.1E-1	Sn-126	1.0E5	3.6E-1
	U-235	7.0E8	1.4E-1	I-129	1.6E7	1.8E-3
	Pa-231	3.3E4	1.9E-6	Cs-135	2.3E6	3.2
			Cs-137	30	2.0E-8	
4	Pu-240	6.5E3	1.9E-1	Sm-147	1.1E11	1.5
	U-236	2.3E7	8.1E-2	Sm-151	93	7.0E-5
	Th-232	1.4E10	5.3E-6	Ho-166m	1.2E3	5.4E-6

**Appendix IIa):** Fission/activation product release rates used for the PG'85 analysis (per canister, 1,000 years after emplacement)

Nuclide	Release rate limited by congruent dissolution		Solubility limited release rate	
	(mol/y)	(Bq/y)	(mol/y)	(Bq/y)
Be-10	5.1E-10	4.2E0	7.1E-5	5.9E5
C-14	3.7E-10	8.5E2	high	-
Ca-41	1.7E-9	1.7E2	7.1E-3	7.2E8
Ni-59	2.2E-7	3.6E4	7.1E-5	1.2E7
Ni-63	3.5E-11	4.6E3	1.2E-8	1.6E6
Se-79	1.8E-6	3.7E5	7.1E-9	1.4E3
Sr-90	1.2E-14	5.5E0	7.1E-5	3.2E10
Zr-93	2.2E-4	1.9E6	7.1E-10	6.3E0
Nb-94	7.6E-9	5.0E3	7.1E-9	4.7E3
Mo-93	1.3E-10	4.9E2	7.1E-3	2.7E10
Tc-99	2.2E-4	1.4E7	2.3E-8	1.4E3
Pd-107	4.9E-5	1.0E5	7.1E-9	1.4E1
Ag-108m	5.5E-13	5.6E1	7.1E-5	7.2E9
Sn-121m	8.2E-16	2.2E-1	8.3E-20	2.2E5
Sn-126	7.0E-6	9.3E5	7.1E-10	9.4E1
I-129	3.5E-8	2.9E1	high	-
Cs-135	6.2E-5	3.6E5	high	-
Cs-137	3.9E-13	1.7E2	high	-
Sm-147	2.9E-5	3.5E0	7.1E-9	8.5E-4
Sm-151	1.4E-9	2.0E5	3.3E-13	4.7E1
Ho-166m	1.1E-10	1.2E3	7.1E-9	7.8E4

**Appendix IIb):** Actinide release rates used for PG'85 analysis (per canister, 1,000 years after emplacement)

Nuclide	Release rate limited by congruent dissolution		Solubility limited release rate	
	(mol/y)	(Bq/y)	(mol/y)	(Bq/y)
Cm-245	6.7E-8	1.0E5	3.2E-5	5.0E7
Am-241	5.3E-6	1.6E8	1.5E-5	4.6E8
Np-237	7.0E-5	4.3E5	1.4E-9	8.7E0
U-233	2.0E-8	1.7E3	2.1E-13	1.7E-2
Th-229	4.0E-11	7.2E1	4.2E-10	7.6E2
Cm-246	6.7E-9	1.9E4	3.3E-6	9.2E6
Pu-242	4.4E-7	1.5E4	3.3E-9	1.2E2
U-238	1.6E-4	4.7E2	1.9E-9	5.6E-3
U-234	2.5E-7	1.4E4	2.8E-12	1.5E-1
Th-230	9.5E-10	1.7E2	1.0E-8	1.8E3
Ra-226	4.7E-12	3.9E1	7.2E-5	6.0E8
Am-243	6.9E-6	1.2E7	2.1E-5	3.8E7
Pu-239	6.0E-6	3.3E6	4.3E-8	2.4E4
U-235	2.8E-6	5.3E1	3.3E-11	6.2E-4
Pa-231	3.7E-11	1.5E1	1.2E-8	4.8E3
Pu-240	3.8E-6	7.7E6	2.8E-8	5.7E4
U-236	1.6E-6	9.0E2	1.9E-11	1.1E2
Th-232	1.1E-10	1.0E-4	1.1E-9	1.0E-3

### Appendix III: Colloids

The formal definition of a colloidal system is deceptively simple - e.g. (from Yariv and Cross, 1979): "Colloid systems may be defined as systems containing at least two components: 1) a continuous dispersing medium and 2) a disperse phase. For many years the science of colloids was concerned mainly with the description of the behaviour of very small particles. The classical definition of a colloid system described the disperse phase as being comprised of particles or macromolecules smaller than 1  $\mu\text{m}$  in diameter, but larger than 1 nm. Particles smaller than 1 nm do not exist as a discrete phase, and any system containing them cannot be considered as heterogeneous."

The colloids of interest in nuclear waste applications are solids dispersed in groundwater for which the classical definition is somewhat ambiguous - the upper limit of 1  $\mu\text{m}$  relates to spherical particles and is not easily related to the irregular shapes of groundwater colloids. Given that the key features of colloids are their surface area/volume ratio and their settling rate, the upper limit of size can be taken to be a hydrodynamic diameter or 1  $\mu\text{m}$  (Ramsay, 1985) which, in soil science, can be taken to give an upper limit of particle size of approx. 2  $\mu\text{m}$  (Yariv and Cross, 1979).

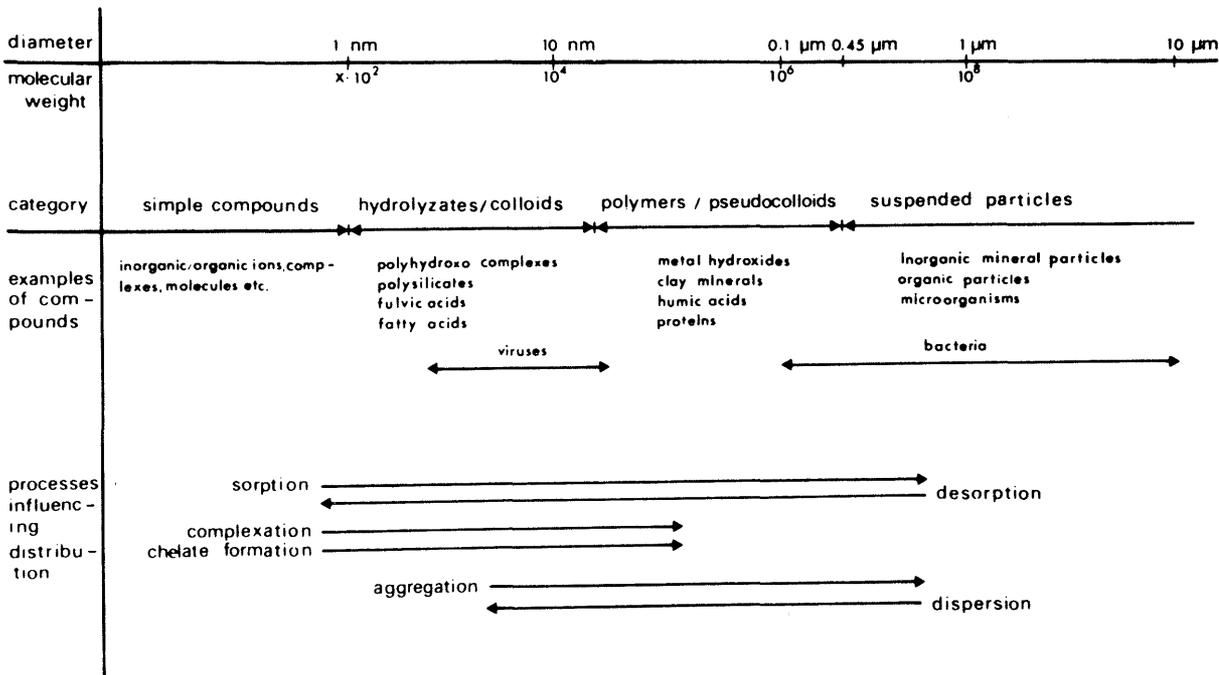
This apparently clear definition is, however, commonly ignored by geochemists with operational cut-offs of colloid/suspended particles usually defined by filter sizes of 0.45 or 0.1  $\mu\text{m}$  (cf. Fig. III-1, Table III-2). It is immediately apparent, therefore, that concentrations of colloidal particles reported in the literature must be treated with great caution and can be very dependent on the particular definition of colloid used.

For safety assessment applications, the limits can be seen in a different light - the lower limit is that at which particles exist as a discrete phase over relevant timescales and the upper limit is that at which filtration along the flow path is approx. 100 % effective. This range thus encompasses mobile particles which have lifetimes with respect to dissolution/-coagulation processes in the order of, at least, years.

The upper size limit is obviously rock formation specific and, in the absence of relevant site-specific data, cannot be generally specified better than as discussed above. The lower limit, however, might be better defined by considering the kinetics of the formation/dissolution of such species at a more fundamental level. The incentive for such an effort is to simplify the analytical problems associated with characterisation of colloids at the lower end of the classical range.

**Table III-1:** Some physical parameters of solutes, colloids and particles likely to exist in freshwater (from Vanderborgh, 1986)

Chemical form binding the metals	Approximate diameter (nm)	Molecular weight range (Daltons)
Small dissolved compounds:		
. hydrated metal ions	<1	<200
. inorganic complex		
. small organic molecules	1-4	<200
Larger dissolved compounds:		
. amino acids	2-4	
. fatty acids	2-6	
. fulvic acids	2-6	200-10 <sup>4</sup>
. polyhydroxo complexes	5-10	
. polysilicates	5-10	
Colloidal material		
. humic acids		
. inorganic colloids (metal hydroxides, clay minerals)	10-100	10 <sup>4</sup> -10 <sup>6</sup>
Suspended particulate material		
. inorganic and organic particles	>100	



**Fig. III-1:** Association of trace elements with compounds in different size ranges. Transformation processes are indicated (from Salbu et al., 1986)

For practical purposes, it is probably sensible to consider organic and inorganic colloids separately. For organics, even relatively small molecules with molecular weights above approx. 200 (e.g. complexing agents such as EDTA) would have sizes significantly over 1 nm. Such molecules plus small oligomers (oligo-peptides, -nucleotides, - saccharides, etc.) can probably be adequately included in current thermodynamic models as "true solutes" and do not need to be considered separately as colloids. In addition, species of this size may be biologically labile and may be readily degraded. Here a cut-off at about 10 nm would seem sensible; smaller species could be considered as part of the "dissolved organic carbon" while the "colloidal organic carbon" would include larger humic acids, poly-peptides, nucleotides, -saccharides, etc. The colloid fraction would need to be considered as a discrete particulate phase.

The smaller inorganic colloids would predominantly consist of oligomers - e.g. oligo-silicates, -hydroxocomplexes. Such species have a very high surface area/volume ratio and tend to be very reactive with respect to dissolution or coagulation processes. An example from the literature (e.g. Laxen and Chandler, 1983) indicates that the lifetime of iron and manganese oxyhydroxides approx. >50 nm in surface waters is approx. 3 months. It may thus be reasonable again to discount inorganic particles <10 nm from consideration due to their short lifetime.