

The chemical basis of near-field containment in the Swiss high-level radioactive waste disposal concept

W.R.Alexander^{1*} & I.G.McKinley²

¹GGWW (Rock-Water Interaction Group), Institutes of Mineralogy-Petrology and Geology, University of Berne, Baltzerstrasse 1, 3012 Berne, Switzerland

²Nagra (Swiss National Co-operative for the Disposal of Radioactive Waste), Hardstrasse 73, 5430 Wettingen, Switzerland

*corresponding author, present address, Nagra (Swiss National Co-operative for the Disposal of Radioactive Waste), Hardstrasse 73, 5430 Wettingen, Switzerland

Abstract. Concepts for the disposal of high-level radioactive waste (HLW) vary from country to country but, in Switzerland, a key contribution to safety is the chemistry of the near-field. In this paper, the development of the Swiss repository design is discussed as a basis for explaining the chemical confinement of radionuclides within the engineered barrier system (EBS). The expected performance of the EBS is described and the chemistry of the system explained. Potential perturbations to the EBS are examined and the methodology of assessing the long-term behaviour of the EBS is briefly described. The relevance of HLW near-field design to chemo-toxic wastes is discussed and an extensive reference list on the chemical aspects of the EBS is provided.

14,890 words, 126 references, 5 figures, 4 tables

In this paper, the chemical basis of containment in one repository design for high-level radioactive waste (HLW), that of the Swiss programme, is examined in detail, focussing in particular on the role of the engineered barriers which constitute the repository near-field (the rock body in which the repository is built constituting the far-field). In addition, the potential relevance of HLW repository design to disposal of long-lived toxic wastes will be discussed.

Before going any further, it is worthwhile briefly considering what constitutes HLW as the precise boundaries between radioactive waste (radwaste) types vary somewhat from national programme to national programme, despite the published IAEA (International Atomic Energy Agency) classifications (IAEA, 1981). HLW consists of spent fuel from nuclear reactors, if a direct disposal option is chosen, or the most active solidified (eg vitrified) residues from the reprocessing of such fuel. Particular characteristics of this waste are its high radiation field which necessitates shielding and/or remote handling, a significant radiogenic heat output, high concentrations of very long-lived radionuclides (half-lives in excess of 1,000 a) and relatively low volumes. For example, a typical package of vitrified reprocessing waste with a volume of 0.15 m³ would have a total radioactivity content of approximately 7x10¹⁵ Bq of β/γ - and 5x10¹³ Bq of α -emitters and a heat output of about 600 W at the time of emplacement in a repository (ie after 40 years surface storage for cooling). The planned 40 a lifetime of the current 5 Swiss nuclear reactors (3GW(e) total) would, however, result in less than 2700 of such packages (around 400 m³ of waste) if all spent fuel was reprocessed. In the UK, in comparison, it is currently estimated that a total of about 2,280 m³ (or almost six times the Swiss total) of conditioned HLW will have been produced by 2030 (Electrowatt 1996).

The low volume of HLW relative to the high value of the electricity generated means that rather over-designed disposal concepts have been developed (see below). Such very expensive options are justified not only by the very strict performance measures imposed in most countries, but also by the general fear of all things radioactive by the general public.

As described in detail by Alder (1997), the reference inventory for a HLW repository in Switzerland constitutes vitrified waste from approximately 1,000 MTHM (Metric Tonnes Heavy Metal) of spent fuel reprocessed at Sellafield (NW England) and Cap de la Hague (N France) and approximately 2,000 MTHM of reactor spent fuel (about 5-10 % will be MOX, or mixed U and Pu oxide, fuel) which may be disposed of directly. In addition, a small volume of high activity, long-lived waste (such as fuel assemblage hulls and ends and as yet unspecified waste from medicine, industry and research) may be included in the Swiss repository.

Derivation of the Swiss HLW disposal concept

Deep geological disposal of HLW is the selected option in all countries with significant nuclear power programmes. A wide range of other options has been studied, but most have been excluded, either for political reasons (eg sub-seabed disposal, Antarctic ice shelf disposal) or due to limitations/costs of current technology (eg disposal in space, transmutation). Even for geological disposal, a wide range of concepts have been studied, but effort is focussed on emplacement in specially constructed underground caverns. A pre-requisite is geological stability, but many potential host rocks have been identified, including crystalline basement, salt, basalt, tuff and a range of argillaceous sediments.

In all cases, a multiple barrier concept has been adopted, but the relative weighting of the engineered barriers and the geological barriers varies (Table 1). As stated above, this paper will be restricted to considering the chemical basis of the near-field of the Swiss HLW repository (although a comparison of designs worldwide is available in Witherspoon 1991, 1996).

To date, the Swiss National Co-operative for the Disposal of Radioactive Waste (Nagra) has carried out three major safety assessments for a HLW repository in crystalline and argillaceous rocks (Figure 1). This paper will concentrate on the near-field chemical containment aspects identified in the two crystalline host rock assessments (Projekt Gewähr and Kristallin-1; Nagra 1985 and 1994a respectively). Note that the near-field of a Nagra HLW repository in sediments would differ only in that the backfill thickness may be reduced and that it also would contain steel tunnel liners (Nagra 1989).

It is, however, interesting to note that Nagra's original HLW repository concept was strongly influenced by that of the Swedish Nuclear Fuel and Waste Management Company (SKB) which was designed without any specific regard to the near-field chemistry. Here, it was planned that the repository tunnels would be situated about 500 m deep in the crystalline bedrock of the Scandinavian Shield. A copper canister (encapsulating spent fuel) would be placed axially in a 1.5 m diameter hole drilled vertically into the floor of the tunnel and the canister would then be surrounded by compacted bentonite and the tunnel backfilled with bentonite and quartz sand (SKB's "in-hole emplacement" concept; KBS 1983).

This design was adapted by Nagra to suit local conditions, resulting in the concept shown in Figure 2. The repository would be situated at between 800-1200 m deep in the crystalline basement of northern Switzerland and, because the original design specifications called for temperatures of <100°C in significant parts of the backfill, an option with a very thick compacted bentonite backfill (or buffer) was selected.

This ruled out the SKB plan for in-hole emplacement and resulted in a design with horizontal emplacement in the tunnel (subsequently, such in-tunnel emplacement has also been studied in Sweden; SKB 1993).

The original SKB design calls for a 10cm thick copper canister, filled with lead, to encapsulate the spent fuel and it was assumed that the copper is so inert under the *in situ* conditions that it will last effectively indefinitely (corrosive penetration in 10-100 Ma). Nagra changed to a massive (25 cm thick walls) steel canister for vitrified waste because the deep groundwater chemistry (in particular, the higher sulphate content) in northern Switzerland will be more aggressive to copper than in the Scandinavian Shield (NWGCT 1984) and a greater mechanical strength was required to withstand the greater external swelling pressures (maximum of 30MPa, the sum of the maximum bentonite swelling pressure and the hydrostatic pressure) as the thin stainless steel fabrication flask containing the vitrified waste contains a void space. In addition, the initial design called for a canister robust enough to last for at least 1,000a to extend beyond early thermal perturbations in the near-field.

Therefore, although the original design reflects a purely engineering approach to the problems of containment, there have been several very clear chemical spin-offs of the final design, namely:

- massive redox (steel canister) and pH (bentonite) buffers ensuring low solubility of radionuclides released from the waste
- colloid filtration due to the microporous nature of the compacted bentonite after resaturation
- diffusive solute transport dominates over advection because of the extremely low hydraulic conductivity of the resaturated bentonite
- high retardation of radionuclides in the buffer due to the good sorptive properties of the bentonite.

Finally, it is of note that the most recent Swiss HLW safety assessment (Kristallin-1) assumes that the near-field will provide the main constraint on radionuclide release and transport and the main role of the geosphere is to provide a suitable environment for near-field longevity and performance. The three most important safety features provided by the geosphere are "...mechanical protection, adequate geochemical conditions and sufficiently low groundwater flow rates" (Nagra 1994a). Precisely how these features impact on the chemical containment of the waste will be discussed below.

Expected Near-Field Performance

The engineered barrier system (EBS) for the Swiss concept is characterised by the use of large quantities of rather simple, well-understood materials. Design optimisation is certainly possible (eg McKinley and Toyota 1998) but has not yet been extensively studied, although the consequences of reducing the diameter of the

emplacement tunnel has been assessed for the crystalline host rock option. Examples of the inventories of materials for vitrified HLW (for two different tunnel diameters) and spent fuel are presented in Table 2. The inventories for the sedimentary host rock option are similar to those for the 2.4 m diameter tunnel crystalline case with the addition of a tunnel liner. Demonstration of the practicality of this concept and development of quality assurance procedures to ensure that emplacement reaches desired standards are amongst the goals of the Spanish implementor ENRESA's (Empresa Nacional de Residuos Radiactivos, S.A., Spain) full-scale engineered barrier system experiment (FEBEX; see McKinley et al. 1996 and Huertas & Santiago 1998 for details) currently running at the Grimsel Test Site, Nagra's underground laboratory in the Central Swiss Alps (Figure 1)

Any repository performance assessment is a large scale undertaking and a wide range of features, events and processes (FEPs) which may effect the overall performance of the repository are identified and linked together into a set of scenarios, each consisting of a sequence of processes and events which describe a possible future evolution of the repository system (see Figure 3). Nagra opted to employ a hierarchy of deterministic calculations to investigate the different types of uncertainty identified in the FEPs examined, but it is beyond the scope of this paper to detail the three Swiss HLW assessments carried out to date. As an example, the Reference Case (see Figure 3) for the crystalline host rock is considered in more depth and, here, the near field is expected to evolve as follows (Nagra 1994a,b):

1). After EBS emplacement, water will begin to resaturate any drained zones of the surrounding rock and then invade the bentonite. As bentonite is contacted by water (by advection through any gaps and diffusion through the rest), it will swell, seal any gaps present and gradually build up an isostatic pressure which is in the order of 4-18 MPa (ie less than lithostatic pressure at the emplacement depth). At the same time, temperatures will increase in the EBS predominantly due to radiogenic heat from the canister (exothermic corrosion and chemical reactions will contribute less than 1% of the heat production) with maximum values being reached within a few tens of years. Evaluation of the development of temperature and water saturation within the bentonite is a complex, coupled problem but models indicate that, while temperatures in excess of 100°C may be expected at the canister surface, these will last no more than a few decades and the majority of the bentonite will remain <100°C (Sasaki et al. 1997). Complete saturation of the EBS will take several (or many) centuries (Andrews et al. 1986) and, because the saturated bentonite has an extremely low hydraulic conductivity (10^{-16} ms⁻¹ to 10^{-13} ms⁻¹), solute transport will occur predominantly by diffusion (Conca et al. 1993). Testing the model assumptions used to develop this description is also an aim of the FEBEX experiment mentioned above.

2) The water chemistry in the near field will be established by interaction of groundwater with the engineered barriers. The two most important materials by quantity (see Table 2) are the bentonite (which will tend to buffer pH in the mildly alkaline range) and the steel canister (which will ensure reducing conditions persist).

Due to very low rates of solute movement in the bentonite and limited solute exchange with low ambient groundwater fluxes (expected to average <1 litre/waste package/year; Thury et al. 1994), the chemistry of porewater is expected to be rather homogeneous and to vary little with time (Nagra 1994a). Very slow alteration of bentonite minerals (sodium montmorillonite, minor calcite, pyrite and siderite) will occur but significant effects are not to be expected within the first 10^6 years (see below).

3) The steel canister will corrode slowly, initially consuming any trapped oxygen in a moist atmosphere and then anaerobically in the presence of liquid water after the bentonite saturates. Based on very pessimistic assumptions, it is calculated that canisters fail mechanically after 10^3 years (NWGCT 1984; Steag & Motor Columbus 1985). More recent analyses indicate that both the corrosion rates considered (McKinley 1991) and the safety margins for the mechanical calculations (Attinger & Duijvestijn 1994) are extremely conservative and a more realistic estimate of the canister lifetime (which is well supported by extensive natural analogue studies, discussed below) would be $\sim 10^4$ years.

Anaerobic corrosion of steel may lead to the production of hydrogen which may form a distinct gas phase. Build up of hydrogen may feed back to further lower the corrosion rate, which can be further encouraged by emplacing a thin sand layer around the canister (Neretnieks 1985). It is considered to be unlikely that gas pressures exceeding the bentonite capillary pressure will be produced. Even if this does occur, it has been shown that gas can flow through compacted bentonite without disturbing its solute barrier properties (discussed below).

Figure 1. Areas under consideration as potential high-level waste repository site in Switzerland. Sites examined for L/ILW disposal and the underground test sites at Grimsel and Mt. Terri are also shown.

4) After canister failure, the waste form will begin to corrode in an environment of stagnant porewater. Vitrified waste dissolves at a very low rate and the corrosion rate is assumed to be constant with time (Grauer 1985). Arguments have been advanced for possible acceleration mechanisms (formation of crystalline secondary products which lower silica concentration and thus accelerate glass corrosion) but long-term

Figure 2. The multiple component engineered barrier safety system for vitrified HLW which constitutes the repository near-field (dimensions in metres).

(~5 year) experiments carried out at the Paul Scherrer Institute, Switzerland (unpublished data) indicate that rates drop to extremely low levels (probably due to the build-up of secondary products on surfaces). Due to the lower density of alteration products and the limited available space within the canister, it is likely that the assumed glass lifetime of $\sim 10^5$ years is very conservative (McKinley 1991). Radionuclides within the waste are assumed to be released congruently with glass matrix dissolution.

Although not considered in detail in Nagra (1994a), it is worth mentioning here the case where spent fuel is disposed of directly (Schneider et al. 1998). This is somewhat more complex as radionuclides are not homogeneously distributed within the UO_2 (or uranium/plutonium mixed oxide in the case of MOX fuels). During reactor operation, some volatile elements (most importantly caesium and iodine) migrate to crystal grain boundaries and gaps between fuel pellets. On contact with water, this inventory is relatively rapidly leached to give a pulse release of activity. Thereafter, radionuclides are released as the fuel matrix dissolves. Additionally, the fuel rod cladding and the structural parts of the fuel assembly contain some activation products which are released in a complex manner as these materials corrode.

Figure 3. Overview of the scenario development methodology employed by Nagra in the Kristallin-1 HLW performance assessment (after Smith et al. 1995)

The fuel dissolution process is very dependent on redox conditions which are, in turn, influenced by the extent of radiolysis of water. Radiolysis is dominated by the α -particle flux and is very sensitive to the available surface of fuel, the geometric distribution of water present, the burn-up of the fuel and the time since emplacement. The chemistry of the water, which critically affects the extent and rate of formation of alteration products, is also of importance. Although there is an extensive database of laboratory studies, there is still some controversy on the magnitude of net dissolution rates under expected conditions. Natural analogue studies of uranium ore bodies indicate that dissolution rates would be at the lower end of those derived from laboratory studies (see below).

5) The release of radionuclides from the waste is constrained, in many cases, by their low solubility. A number of simplifications are made because of the limitations of current models/databases for quantifying solubility limits (McKinley et al. 1988).

- Solubility limits are defined for a water chemistry which would correspond to bentonite porewater with redox conditions buffered by canister corrosion products. Although based on the reference bentonite porewater compositions, uncertainties in host rock groundwater composition are also taken into account.
- A chemical thermodynamic model is used to assess solubility limits for a range of pure mineral phases which could potentially form under the expected conditions. Note that the calculations were carried out at 25°C as, first, relevant data are rare for higher temperatures and, second, other uncertainties in the calculations are much larger than any temperature effect on the solubilities.
- The output of the thermodynamic model is reviewed in terms of literature data on the formation of identified minerals and measured concentrations of the element of interest in relevant natural and laboratory systems.
- The likelihood of formation of pure phases is assessed in terms of the relative inventories of elements with similar chemical properties in the waste.
- Bearing in mind the intention to err on the side of conservatism in the derivation of parameter values (ie over-prediction of solubility limits), expert judgement is used to select elemental solubility limits which are defensible as "realistic-conservative" (reasonable, but pessimistic in the handling of uncertainties) and "conservative" (worst case based on all available data) values.

The procedure and results of this selection procedure are documented in Berner (1994); a simplified overview of the main considerations involved in the selection of solubility limits for specific elements is given in Table 3 and the resultant limits for the safety assessment are listed in Table 4.

Due to chemical buffering by the canister corrosion products and bentonite minerals (particularly pyrite and siderite), it is not expected that the oxidising conditions, which may form at the surface of spent fuel, will have a significant influence on the rest of the EBS (Smith & Curti 1995). In this case, the solubility limits derived for the vitrified waste case can be directly applied – a redox front may exist within the canister corrosion products or bentonite but this will not influence releases from the near-field to the geosphere. Extensive precipitation may occur at this redox front which may initially be in the form of colloids. The small pore size (average ~2-10 nm, Pusch 1980; McKinley 1988) of the compacted bentonite should ensure that any colloids formed are immobile in this medium, something which has recently been verified experimentally (Kurosawa et al. 1997). It should be emphasised that this situation contrasts to designs with a chemically inert canister and small bentonite annulus (eg in Sweden) where the redox front is calculated to pass through the EBS and penetrate the geological barrier (Romero et al. 1995).

6) The diffusion of dissolved radionuclides through corrosion products of the waste form and canister and the surrounding bentonite will be retarded by sorption on the solid phases present (which is distinguished mechanistically from precipitation/ co-precipitation processes considered above – cf McKinley & Alexander 1996). Even though it is likely that canister corrosion products may act as powerful sorbing agents, performance assessment concentrates on the rôle of bentonite due to its larger inventory and greater confidence in its general availability. Note that canister failure would be localised which would limit the surfaces available to migrating nuclides – although in such a case the transport resistance of the crack involved could be significant (Smith & Curti 1995).

Based on numerous batch sorption and diffusion experiments, several extensive databases exist on solute transport through compacted bentonite (eg Stenhouse 1995; Yu & Neretnieks 1997). Although this clearly indicates significant retardation of many key elements, the lack of a simple correlation between sorption experiments carried out on dispersed bentonite and diffusion studies on highly compacted material has caused some confusion (Stenhouse 1995, Appendix A; Conca et al. 1993; Yu & Neretnieks 1997). A consensus is presently emerging that compacted bentonite is probably better represented as a micro-porous charged membrane than a dispersed mineral assemblage. Nevertheless, regardless of the mechanisms involved, a simple sorption model can be applied to the large empirical database and shown to be conservative in that migration is over-predicted. Transport calculations using the performance assessment sorption database (Table 4) indicate that a large proportion of the radionuclide inventory of the waste decays to insignificance within the engineered

barriers. Very long-lived radionuclides, which do eventually break through the bentonite barrier, generally do so only in the far future and at levels which are radiologically insignificant (Nagra 1994a; Smith & Curti 1995).

The safety of this disposal concept is illustrated for vitrified HLW in Figure 4a which shows that, with rather pessimistic assumptions about performance of the geological barrier, releases occur only in the far future and are orders of magnitude below regulatory guidelines (Nagra 1994a). Similar performance is indicated for the case of direct disposal of spent fuel (see Forsyth 1995; Schneider et al. 1997), although analyses carried out to date have been less extensive and, as such, will not be described in detail here.

More dramatically, perhaps, Figure 4b also shows the direct effect of the EBS by "switching out" the geosphere and allowing releases from the near field to pass directly to the accessible biosphere. Although releases of less well retarded nuclides occur at earlier times and integrated releases are higher, dose limits remain well below regulatory guidelines at all times. It is much more difficult to carry out the same exercise in reverse: first the geosphere is much harder to define as precisely as the EBS and, second, it is almost impossible to define a sensible source term. Nevertheless, scoping calculations have been carried out assuming unit releases for specific radionuclides and several points are worth noting:

- the choice of geometrical representation of water-conducting features is critical to the calculated performance of the geosphere. Determining which features dominate radionuclide transport and accounting for their complex nature with appropriate models are "...key areas for future work." (Nagra 1994a).
- the variability of flow between water-conducting features can also significantly effect the overall performance of the geosphere by adding additional dispersion.
- currently, whether modelling retardation of radionuclides in water-conducting fractures or assessing the influence of colloids on dose to the biosphere, a lack of detailed data means that conservative representations are always employed. Only with the production of additional data will it be possible to justify a less conservative representation of the geosphere, so increasing supportable safety margins and allowing optimisation of the repository concept.

The key parameters which determine near-field performance are:

- ♦ Canister lifetime
- ♦ Glass corrosion rate
- ♦ Elemental solubilities
- ♦ Elemental sorption on bentonite
- ♦ Groundwater flux around the engineered barriers

These are now considered in turn, emphasising the effects of selecting more conservative values. The canister lifetime (in terms of loss of containment) of 10^3 a is considered to be very conservative with respect to the assumed corrosion rate which is, in itself very conservative in the light of natural analogue data (discussed below). The canister design and subsequent evaluation of the canister performance is discussed in Nagra (1984) and Steag & Motor Columbus (1985) and failure in less than several hundred years is considered extremely unlikely (even then this would have little significant effect on releases due to the constraints set by the slow dissolution rate of the glass waste-form and the powerful barrier rôle played by the bentonite). In addition, the original analysis has been verified and tested against experiments, including the prediction of failure of scale-model canisters in the European Community COMPAS exercise (Ove Arup 1990; Attinger & Duijvestijn 1994). Even less likely is the case of failure soon after emplacement (within 100a, say) due to manufacturing flaws as fabrication quality should be ensured by the use of a simple production methodology (sand-mould casting) and ultrasonic inspection of the completed canister, lid and weld. In any case, early failure would not be expected to increase doses significantly, although the applicability of the simple release model could be questioned due, for example, to the higher temperatures and significant thermal gradients which are present.

The release model would, however, probably be very conservative at such times as the inner zone of the bentonite would still be in the process of resaturation. The waste-form would thus not be exposed to liquid water and, in addition, a net flux of water towards the canister would be expected to prevent outwards radionuclide transport.

The glass corrosion rate chosen was based on an extrapolation of laboratory experiments and is believed to be reasonably conservative but calculations were repeated assuming a value 2 orders of magnitude higher. The release rates of most radionuclides are, in any case, constrained by their low solubilities and hence are unaffected by this change. A notable exception is ^{135}Cs which is not solubility-limited. The maximum ^{135}Cs release concentration from the near-field does not scale linearly with the glass corrosion rate, however, due to dispersion (ie spreading of the peak) during transport through the bentonite, which means that the increase in resultant dose is only by less than one order of magnitude. Calculated doses are, therefore, still well below the regulatory guidelines.

Elemental solubility limits are a very important constraint on the releases of many radionuclides and selecting a set of more conservative values of this parameter significantly alters the profile of calculated doses as a function of time. Decay during near-field and geosphere transport minimises the consequences of such

changes for some nuclides as does the fact that, as solubilities increase, the glass corrosion rate takes over as a constraint on releases.

There is a fairly large body of experimental data to support selection of "realistic" elemental diffusivities (derived both from the sorption and diffusion measurements) for the bentonite backfill. Repeating the calculations with more conservative sorption distribution coefficients (generally a factor of 10 smaller) has little effect on calculated releases from the geosphere, even though the near-field release profiles change somewhat. A major effect of such increased diffusivity is to allow release from the bentonite of some isotopes which otherwise decay within the near-field (^{59}Ni , ^{126}Sn , ^{239}Pu , ^{242}Pu). However, these radionuclides are not dominant contributors to dose and, in any case, will decay within the far-field.

The rate of diffusion through the backfill is influenced by the rate at which dissolved species can be removed from its outer surface which is related, in turn, to the water flux around the engineered barriers.

The sensitivity of releases to this parameter was evaluated by repeating calculations assuming one or two orders of magnitude higher fluxes. Considering the near-field only, calculations show that increasing the flux by a factor of 100 causes an increase of the maximum release rate of ^{135}Cs by a factor of only about 5, although the maximum is reached at an earlier time ($\sim 10^4$ a rather than $\sim 10^5$ a). Increasing the flux has a more dramatic effect on releases of other radionuclides. For example, the release rate of ^{79}Se initially increases almost linearly with water flux, although this drops off somewhat at higher fluxes. Considering the full waste inventory shows that, even for 2 orders of magnitude higher flux, the regulatory guideline would not be reached.

The general conclusion is, therefore, that the EBS for HLW is "robust" (McCombie et al. 1991) in that expected performance based only on well-understood processes meets performance guidelines even if very pessimistic assumptions are made about poorly-understood processes or potential perturbations.

Potential perturbations to the near-field

The previous section makes the case that the system of engineered barriers considered is "robust"; in order to justify this it is necessary to demonstrate that all conceivable processes which could cause degradation of performance have been assessed. As noted in the sensitivity studies, if the bentonite buffer, canister and waste form behave as expected, then safety goals can be met even if very pessimistic parameter values are assumed. The critical question is, therefore, can the occurrence of processes which could short-circuit one or more of the multiple safety barriers be rigorously precluded? It was noted in the Kristallin-1 safety assessment that "...most phenomena that could be detrimental to safety are excluded or forced to low probability or consequence by the

repository design and siting concept." (Nagra 1994a). This is aided by the use of relatively well understood materials within the EBS which are then further tested to assess their behaviour under repository specific conditions.

In most engineered systems, such as bridge construction, this would include a range of laboratory experiments backed up by expert judgement based on experience with the same or similar systems. Here repository design deviates from standard engineering practice in that no HLW (and only a few L/ILW) repositories yet exist and, when they do, testing their compliance to design limits will be somewhat difficult due to the time scales involved. This being the case, an additional level of testing has been developed within the radwaste industry, that of the natural analogue approach (see Chapman et al. 1984; Chapman & McKinley 1987,1990; Miller et al. 1994).

Briefly, a natural analogue may be defined as "...(*a natural or archaeological*) occurrence of materials or processes which resemble (ie *are analogous to, but not copies of*) those expected in a proposed geological waste repository." (Côme & Chapman 1986). The advantage of natural analogues over short-term laboratory experiments or medium-term in situ field tests is that they enable study of repository-like systems which have evolved over the geological timescales of relevance to a radwaste repository safety assessment (rather than the days to months usual in laboratory tests). However, by their very nature, natural analogues often have ill-defined boundary conditions which means that some specific processes may be better assessed under the well constrained (if less relevant) conditions of a laboratory. Well designed, realistic in situ field tests can bridge the gap between the laboratory and natural analogues by offering repository relevant natural conditions with some of the constraints of the laboratory (and intermediate timescales). In short, combining information from the three sources (long-term and realistic, if poorly defined, natural analogues, medium-term, better constrained, in situ field tests and short-term, less realistic but well defined laboratory studies) can provide greater confidence in the extrapolation of laboratory derived data to repository relevant timescales and conditions (Alexander et al. 1998). In the following sections, this approach is used to assess the significance of several potential perturbations to the chemical containment of waste in the repository near-field.

Bentonite

The thick layer of compacted bentonite plays a key rôle in the near field, ensuring that solute transport occurs by diffusion and that colloid migration is precluded. Extensive review efforts (Nagra 1994a) have identified several potential perturbations which could, potentially, have a major influence on this barrier function:

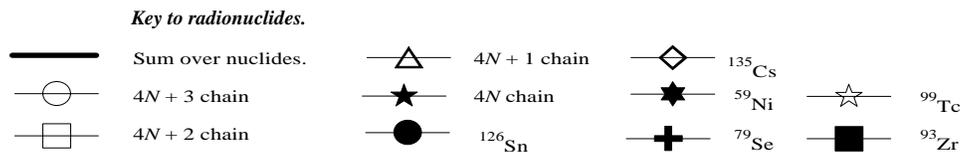
- ♦ Mineralogical alteration of the bulk bentonite so that its plasticity, swelling pressure and microporous structure are lost
- ♦ Cementation and subsequent fracturing of the bentonite without significant alteration of the bulk bentonite
- ♦ Sinking of the canister through the bentonite
- ♦ Physical perturbation of the bentonite due to gas (H₂) produced by anaerobic corrosion of the steel canister.

These processes are now addressed in turn:

Bentonite alteration: A review of the existing literature on laboratory data suggests that the long-term stability of the bentonite (at repository ambient temperatures of 40 - 55°C) is most likely to be compromised by the possible alteration of montmorillonite to illite (note that alteration to chlorite is extremely unlikely due to the low magnesium levels of the deep crystalline groundwaters). This would have the two-fold effect of reducing both the swelling potential (possibly allowing advective flow through gaps in the bentonite and reducing colloid filtration) and the cation-exchange capacity (CEC) of the bentonite (so decreasing radionuclide retardation in the near-field).

The montmorillonite/illite transformation will only occur when the tetrahedral layer charge of the clay increases and the interlayer ions are replaced by potassium ions. However, increasing the layer charge alone does not change the swelling capacity, the presence of interlayer potassium ions is also necessary (Grauer, 1990), ie the supply of potassium to the bentonite can limit illitisation. This being the case, the degree of

Figure 4. Time development of the annual individual doses in the safety assessment Reference Case. Upper figure: results of the Reference Case calculations. Lower figure: as an illustration of the effect of the EBS alone, the hypothetical case of direct release of radionuclides from the near-field to the biosphere is also presented.



bentonite alteration can be estimated based on the site characterisation data on deep groundwater chemistry (potassium concentration), regional hydrology (groundwater flux) and the likely long-term evolution (increased or decreased potassium concentration or groundwater flux) of the deep groundwater system.

In the case of a repository in one of the two potential siting areas in the crystalline basement of northern Switzerland (Figure 1), total conversion of montmorillonite to illite was calculated to take between 10Ma (eastern site; McKinley 1985) and 100Ma (western site; Nagra 1994a). For the latter site, even assuming that the groundwater flux is two orders of magnitude higher than the (already conservative) reference flux and assuming that all potassium in the groundwater is taken up by the montmorillonite, the bentonite buffer can still be expected to carry out its barrier role for more than 1 Ma.

Even if it was the case that the potassium supply was unlimited, then the rate of increase in layer charge may be assumed to control illite formation. Illitisation in this case is strongly kinetically hindered and is difficult to study in the laboratory under relevant conditions. It has been stated that illitisation does not occur at all below 60°C and is negligibly slow below 100°C (Anderson 1983). Although it was noted in Nagra (1994a) that such an extrapolation is not easy to defend due to the large degree of uncertainty regarding the temperature dependence of the activation energy (E_a) of illitisation, data from natural analogue studies (Yusa et al. 1991) have increased confidence in the laboratory data, producing E_a values of 27 kcal mol⁻¹, close to the 30 kcal mol⁻¹ of Roberson & Lahann (1981).

Nevertheless, several open questions remain on the long-term behaviour of the bentonite buffer and so Nagra has considered natural analogue studies of montmorillonite-rich systems of relevant ages to lend support to the predictions. On the question of the likely degree of illitisation of montmorillonite, studies of diagenetic illitisation in the clays of the Gulf of Mexico (eg Eberl & Hower 1976; Roberson & Lahann 1981; Müller-Vonmoos & Kahr 1985; Freed & Peacor 1989) and elsewhere (Pusch & Karland 1988) indicate that the rate of illitisation in nature is much slower than predicted by kinetic models (eg Anderson 1983) and that even if the supply of potassium was much higher than expected, complete illitisation of the buffer material can be ruled out within the timescales of relevance to the performance assessment (~1Ma) for the given repository conditions.

Thermal effects: in certain repository designs, the canister/bentonite contact may reach several hundred degrees Celsius but, as noted above, in the Nagra concept the maximum temperature should peak at about 150°C and no more than a third of the total thickness of the bentonite should be exposed to temperatures in excess of 100°C for more than a few decades. During this heat pulse, some alteration of the bentonite may be expected: for example, the experimental work of Pusch & Karnland (1990) shows that between 130°C and 150°C all interlayer water is expelled and shrinkage cracks may form. However, Oscarson et al. (1990) report that such shrinkage cracks are reversible and heal following resaturation, as would be the case in the Nagra repository following the short, initial heat pulse.

The effect could be significant only if the CEC of the montmorillonite is saturated with potassium during the maximum temperature pulse (temperatures >110°C are necessary) but this is excluded due to the low potassium flux at the proposed site (see comments above). In addition, the heat pulse will, in any case, coincide with the period of resaturation of the compacted bentonite following repository closure (ie there is unlikely to be significant groundwater in the high temperature zone of the bentonite at that time).

It is, however, possible that water vapour may exist in the bentonite if a significant thermal gradient still exists during resaturation. Interaction of the vapour with the compacted bentonite has been observed to cause cementation with an associated loss of some of the swelling capacity (Couture 1985). This has been studied further in the laboratory (eg Meike 1989; Pusch & Karnland 1990; Pusch et al. 1992) and, while significant cementation can occur within the first few centimetres of the heat source, compacted bentonite outwith this zone shows no appreciable change in properties.

The effect can be minimised by careful choice of appropriate densities of the dry bentonite, so ensuring the remnant swelling capacity is sufficient to ensure low permeability of the bentonite (see Grauer 1990). Interestingly, the cementation appears to be caused by secondary sulphates in the hottest (near canister) zone, followed by amorphous silicates further away from the canister, with no evidence of secondary iron phases resulting from bentonite/canister interaction (Pusch et al. 1992). This work backs up that of Müller-Vonmoos et al. (1991) who carried out short-term (ie six to seven months duration) experiments with iron- and magnetite-bentonite mixtures at 80°C and found no significant changes to the bentonite. Nevertheless, canister/bentonite reactions could occur in theory (although insufficient thermodynamic data exist to fully assess the problem), leading to the production of the iron silicates chamosite, greenalite and nontronite (Grauer 1990). However, even assuming all of a canister reacted with the bentonite to form such phases, only a maximum of 20 % of the

montmorillonite in the buffer in the immediate vicinity would be effected and the changes to the total swelling capacity and sorption capacity would be insignificant (Nagra 1994a).

Heating effects have also been examined via natural analogue studies, the most detailed being that of Pusch et al. (1987) on smectite-rich clays (as an analogue for montmorillonite). The authors concluded that, despite high temperature cementation, a remnant smectite content of 15-25 % will ensure a reasonable self-healing ability. Pusch & Karnland (1988) also noted that, at around 150°C, cementation can occur, work which has since been verified in the laboratory (Pusch and Karnland 1990). Further natural analogue studies of high temperature cementation in clays (in NW Scotland and N Italy) are currently ongoing within the radwaste programme of the European Community (the results of which will be published within 1998) and ENRESA has begun work on natural bentonites in southern Spain.

Finally, it is of note that ENRESA are also currently (the experiment officially began in November, 1996) carrying out a five year, full-scale field test of the near-field multi-barrier system in Nagra's underground test site at Grimsel in the Swiss Alps (McKinley et al. 1996; Huertas & Santiago 1998). It is hoped that this experiment and a complementary 2/3 scale laboratory study, both of which use heaters to mimic the heat flux from a real canister, will be able to confirm some of the small-scale, shorter-term laboratory experiments (eg on the effects of water vapour on the compacted bentonite) and act as a bridge between the short-term laboratory data and the information obtained from natural analogues.

Physical perturbations: although this paper addresses mainly chemical processes, there are a couple of physical perturbations of the bentonite buffer which are worth briefly mentioning: canister sinking and gas disruption.

If the bentonite is to be an effective part of the EBS, it must completely surround the canister over a very long period of time. If the canister were to sink through the bentonite, under gravity, the full effectiveness of the bentonite could be compromised. In Kristallin-1, it was calculated, on the basis of the short-term laboratory data of Börgesson et al. (1988), that the canister would sink no more than 1-5 mm in 10,000 a, an amount that is negligible for the safety of the repository. However, potential shortcomings in the calculations, including use of a model developed to study creep in soils and use of parameters from non-bentonitic clays (S. Horseman, pers. comm., 1994), led Smith & Curti (1995) to re-examine the question. Rather than attempt to re-calculate the extent of sinking using another model, their approach was simply to assume significant sinking (69 cm, or half way to the tunnel floor) and calculate the likely impact on radionuclide release. For this scenario, they found

that, for certain critical radionuclides, a maximum 20 % increase in release from the near-field to the repository host rock was possible, resulting in negligible radiological consequences.

Nevertheless, due to the importance of the bentonite buffer to the near-field performance and lack of evidence that the short-term laboratory results can be safely extrapolated to repository timescales (it has so far not proved possible to find an appropriate natural analogue to provide long-term data in support for the laboratory results, although ENRESA are currently examining a possible site in S Spain), design modifications (eg incorporating a sand-rich layer around the canister or placing stone supports under the canister) have been considered (Nagra 1994a; McKinley & Toyota 1998).

The production of hydrogen by anaerobic steel corrosion is the most significant source of gas in the near-field. Recent experimental work indicates a gas production rate of 0.02 to 0.2 mol m⁻² a⁻¹ while the maximum loss of hydrogen from the canister surface by aqueous diffusion is approximately 0.02 mol m⁻² a⁻¹ (Nagra 1994a). Thus it is possible that a free gas phase could be produced at the canister/bentonite interface and that this phase could be vented when the gas pressure reaches 30-70 % of the bentonite swelling pressure (Pusch et al. 1985). The gas is presumably released by the creation of channels through the bentonite and this behaviour has been recreated by the model of Grindrod et al. (1994) which shows that the gas probably passes through connected capillary pores of 10nm in diameter, consistent with the estimate of minimum effective diameter of connected porosity in the bentonite buffer (McKinley 1988).

If this is the case, no significant physical disruption of the bentonite seems likely (and thus no loss of the buffer's radionuclide retention properties). Certainly, laboratory experiments on the process in consolidated clays (e.g. DeCanniere et al. 1993; NEA, 1992) have indeed shown that the channels are difficult to detect afterwards other than by X-ray tomography. Nevertheless, it was mentioned in Kristellin-1 that the study of hydrogen evolution and potential disruption of the bentonite should be kept under review and it is worth noting that similar tests on compacted bentonite are currently underway in Japan (PNC 1993) and in the UK (funded by the so-called GAMBIT Club) to further assess the extent of the process.

Canister

The main perturbations associated with the massive steel canister are canister failure through corrosion, hydrogen gas production due to anaerobic corrosion and redox changes around the canister following canister failure (Nagra 1994a). Gas has already been treated above and the discussion here will concentrate on corrosion processes during the first 1,000a after repository closure (when complete containment is assured) and the role of corrosion products as redox buffers.

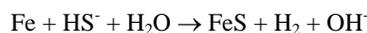
In Nagra's Projekt Gewähr safety assessment (Nagra 1985), three particular corrosion processes were considered to be of potential significance:

1) Reaction of the canister with oxygen trapped in the EBS (mainly in the bentonite pore spaces) at the time of emplacement in the repository.



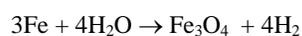
Per canister, approximately 9.3 kg of oxygen are available at repository closure (NWGCT, 1984) and, assuming that all of the oxygen trapped reacts only with the canister (and not with, for example, pyrite in the bentonite) within the 1,000a period (discussed above), a maximum of 32 kg of iron (as cast steel) can be corroded. This corresponds to an average depth of corrosion over the entire canister of 0.7 mm.

2) Reaction with dissolved sulphides produced from reduction of sulphates in the groundwater.



When it is conservatively assumed that all sulphate available in the groundwater and the bentonite will be reduced to sulphide by bacteriological action and is thus available for corrosion (Nagra 1984), and that the reaction rate is extremely fast (rate limiting step assumed to be transport of corrodant to the container), then a maximum amount of 173 kg of steel per container will be corroded in the first 1,000 a (NWGCT 1984). This corresponds to an average depth of corrosion over the entire canister of 3.8 mm. Re-examined today, these calculations are seen to be even more conservative than was realised at the time as improved deep groundwater sampling techniques indicate groundwater sulphate contents 3-6 times lower than stated in the original work (cf NWGCT 1984 and Pearson and Scholtis 1993).

3) Anaerobic reaction with water.



The long-term corrosion rate of iron in the anaerobic, sulphide-free, saline waters representative of the host

Fig. 5. Corrosion rate data from natural and archaeological analogue studies (after Miller et al 1994). The corrosion rates for the archaeological artefacts range from 0.1 to 10 $\mu\text{m a}^{-1}$ (note that samples 1 and 2 are from oxidising marine conditions; details of all other samples included in Johnson & Francis 1980). The Nagra base case corrosion rate for steel canisters from Projekt Gewähr is also shown for comparison

rock at repository depth was calculated on the basis of a variety of laboratory tests (eg ONWI 1983; Marsh et al.1983; Simpson 1983, 1984). The experiments generally showed an initial high corrosion rate(30-70 $\mu\text{m a}^{-1}$) which rapidly decreased to 5-10 $\mu\text{m a}^{-1}$ and is independent of the radiation doses expected at the glass surface in the Swiss design. Simpson (1984) concluded that a conservative corrosion rate, including an allowance for pitting, was 20 $\mu\text{m a}^{-1}$, giving a maximum depth of 20 mm in 1,000 a. In addition to this, NWGCT (1984) included a pitting allowance of a factor of two in the corrosion depths calculated for the reactions with oxygen and sulphide (ie 9 mm rather than 4.5 mm in 1,000 a) giving a maximum conservative corrosion depth of 29 mm in the critical 1,000 a period.

Canister stress and stability analyses have shown that a canister suffering pitting corrosion to a depth of 50 mm will still survive the maximum external isostatic pressure of 30 MPa (Steag & Motor Columbus 1985), indicating that the conservative assessment of 30mm canister corrosion in 1,000 a still leaves a high margin of safety in the design.

As an additional check on the long-term performance of the canister, Nagra has carried out natural and archaeological analogue studies of iron artefacts from a range of environments (see NWGCT 1984; Miller et al 1994). Despite the fact that most material studied came from oxic to sub-oxic environments and would therefore be expected to corrode to a much greater extent than in the oxygen-free repository setting, a maximum corrosion depth of 10 mm in 1,000 a has been calculated (Figure 5), so increasing confidence in the results from the short-term experimental data and the Base Case assumption of 29 mm.

The Kristallin-1 assessment assumes that, following failure, the canister offers no retardation to radionuclides leaching out of the vitrified waste. In reality, of course, failure of the canister will be localised and the resultant crack or hole may be the only route from the glass to the bentonite. This will be a beneficial effect (compared to the assumptions made in Kristallin-1) as the crack will offer transport resistance to the leached

radionuclides (Smith & Curti 1995), but a possible detrimental effect would be the release of oxidants produced by the radiolysis of water in contact with the vitrified waste. If the radiolytic oxidants were to pass through a crack in the canister which was coated by non-porous ferric oxides, so minimising reaction with the bulk of the canister steel, the oxidants could penetrate to the bentonite so leading to a loss of reducing conditions in the bentonite pore waters and consequently to higher solubilities (see Wanner 1985; Berner 1994) and lower sorption (see Stenhouse 1995) for certain redox sensitive radionuclides.

This scenario has been examined by Smith & Curti (1995) who found that, in the worst case (ie using high estimates of radiolytic oxidant production, low estimates of iron in the bentonite to soak up the oxidants etc.), the oxidation front would be unlikely to penetrate more than 2cm into the bentonite buffer and so would not lead to any greater loss of radionuclides from the near-field. Even this assumption is arguably over-conservative on two grounds: first, this does not take into account the likely uptake of at least some of the radionuclide flux at the redox front in the bentonite. Such redox retardation at fronts is well documented in natural conditions (see the review of Hofmann 1998), a good example being the concentration of uranium (up to ore grade) in the so-called roll-front deposits which are so common in southern USA. Second, the canister itself will likely act as a redox buffer and can readily consume all possible oxidants produced by radiolysis of water by vitrified waste (McKinley 1985).

Waste form

1. Vitrified waste

The Kristallin-1 safety assessment notes that the most likely perturbation of the glass would be the production of colloids, containing radionuclides, as the glass degrades/dissolves. However, as long as the bentonite buffer remains functional, the colloids should be filtered out in the very fine pore structure of the bentonite. Both laboratory and natural analogue data (reviewed in Lutze 1988, and Miller et al. 1994, respectively) suggest that the rate of devitrification of the glass is too slow to be a significant problem (although, arguably, the effect of radiation on long-term devitrification rates should be checked by appropriate natural analogue studies). Existing laboratory data suggest that the glass lifetime of 10^5 a assumed in Kristallin-1 is conservative and natural analogue studies indicate up to 10^7 a. However, differences in the chemistry, thermal history and radiation dose rates of natural glasses and vitrified waste means that, according to Miller et al. (1994), "...natural glasses offer no unambiguous evidence for the time at which devitrification begins, or the rate at which it proceeds, although the existence of natural glasses millions of years old may suggest that devitrification is not a problem".

2. Spent fuel

Although several major assessments of spent fuel disposal concepts have been carried out (eg Antilla et al.1982; KBS 3 1983; SKB 91 1992; Vieno et al. 1992), Nagra have carried out only preliminary assessments to date (Nagra 1985; Schneider et al. 1997). Other than the potential scenarios already discussed above for other components of the EBS which may have an impact on the spent fuel (eg redox front propagation through the bentonite buffer), the most significant potential perturbation identified so far relates to radiolytically induced dissolution of the fuel matrix (Forsyth 1995). Despite an extensive laboratory based data-set (eg Forsyth and Werme 1987, 1992; Bruno et al. 1995; Loida et al. 1995), the fact that much of the data has been produced using only model solutions means that uncertainties remain in the likely rate of radiolysis under near-field conditions (Johnson et al. 1994).

Consequently, the safety assessments carried out to date have been based on very conservative assumptions. For example, in the Finnish programme, the rate of radionuclide release from the spent fuel matrix is based on data measured under oxidising conditions, even though more realistic experiments (with reducing conditions in the test vessel, if not at the fuel surface) show release rates which are a factor of ten lower (Vieno et al. 1992). The release of radionuclides from the gaps and the grain boundaries is generally modelled as being instantaneous following canister failure (eg Schneider et al. 1997), but there is some uncertainty in the radionuclide inventories at these locations, especially for high-burnup UO₂ and MOX fuels.

Although in all studies to date the calculated doses to the public remain below the respective national exposure limits, use of more realistic data would undoubtedly boost public confidence in the validity of the assessments. Once again, the problem is obtaining data which realistically can be extrapolated to repository conditions. To this end, many uranium ore bodies have been examined as natural analogues of spent fuel disposal (see review in Miller et al. 1994). Arguably, the most relevant of these studies has been the work carried out at the 1.3Ga Cigar Lake ore body in Canada (see Cramer & Smellie 1994) and at the ~2Ga Oklo natural reactors in the Gabon (Blanc 1996). The conclusions of a recent reappraisal of the Cigar Lake study (Smellie & Karlsson 1996) were that "Studies of water radiolysis at Cigar Lake showed that the net changes in the ore and near-field were considerably overestimated by models currently used by performance assessment to calculate the yield of radiolysis products." and "These results appear to support the (*apparent*) inadequacy of current performance assessment radiolysis models as applied to Cigar Lake where the calculated oxidant production rates are significantly higher (*than was observed at the site*).".

Simple studies of the magnitude of the effects caused by radiolysis have been carried out also at Oklo (Curtis & Gancarz 1983). Much information is also available on the fate of radionuclides associated with the uranium ore 'fuel' (eg Gancarz et al. 1980; Curtis 1985; Brookins 1990; Blanc 1996). Some dissolution and elemental remobilisation occurred, but the fact that more than 90% of the uranium has remained in the same place since criticality and that little uranium ore/groundwater interaction has been observed under the present day conditions (as opposed to the much higher temperatures during criticality) lends qualitative support to the conclusions of the Cigar Lake study that the current performance assessment models of spent fuel dissolution are extremely conservative.

Other potential perturbations

1. Microbiology

The early ideas that a radwaste repository would provide too harsh an environment for microbial life were quickly proven wrong for both HLW (eg Mayfield & Barker 1982; West et al. 1982; West & McKinley 1985) and L/ILW (eg Francis et al. 1980; Francis 1982; McGahan 1987; West et al. 1992; Coombs et al. 1998). Nagra, among others (eg Stroes-Gascoyne 1989, in Canada; Colasanti et al. 1991, in the UK), has attempted to assess quantitatively the likely impact of microbes on the chemistry of the repository near-field (McKinley et al. 1985). Microbiological activity, with the associated production of organic complexants, could reduce the effectiveness of the EBS by increasing the solubility of radionuclides in the near-field (by organic complexation, for example) and decrease sorption on the buffer and canister.

In the case of a HLW repository, the relative simplicity of the EBS allows reasonable constraints to be placed on the maximum likely microbial activity, which will be tightly constrained by the low supply rates of nutrients and the low availability of usable energy. According to McKinley and Hagenlocher (1993), the maximum steady-state biomass production for a Swiss HLW repository in northern Switzerland would be 10^{-5} kg (dry) a^{-1} per waste package and, in the worse case, this biomass production would be balanced by a similar rate of production of organic complexants. This would be some three orders of magnitude more organic carbon than would be available from the groundwater. However, even when building worse case upon worse case by assuming that the organic carbon is present only as extremely strong specific complexants such as siderophores, that these are not filtered by the bentonite due to their very small size and that all the organics complex only with

actinides in the waste, this would only approximately double the maximum release rate of actinides. Considering the other uncertainties involved in estimating near-field solubility limits, this is an insignificant increase.

One potential weakness in the above approach is that the effects of interfaces (pH/Eh) and heterogeneities in the EBS are ignored. This has been tackled recently by McKinley et al. (1997) who noted that their more thorough analysis "...gives a more realistic evaluation of possible microbial perturbations (*of the HLW near-field*) which indicate that the net effect of such populations may be positive, leading to decreased radionuclide release (*due to uptake in and around the fronts*). The critical assumption, however, is that microbes cannot utilise the very low energy density of the reaction between steel and water." The conclusion that microbial activity could contribute to radionuclide retention is well supported by natural analogue studies which have shown that trace element traps, such as redox fronts or haloes, are established by microbially catalysed reactions (eg West et al. 1992; Hofmann 1998).

The extremely stable Cigar Lake uranium ore body also exists in an environment where relatively high microbial populations have been measured (Stroess-Gascoyne et al. 1994) and Smellie & Karlsson (1996) noted that the bacteria present are probably playing a role in stabilising the ore via consumption of oxidants produced by radiolysis.

2. Groundwater disturbances

It was noted in the introduction that the geosphere must offer mechanical protection and hydrogeochemical stability to the EBS to ensure performance of the system. The potential HLW sites in Switzerland (Figure 1) are felt capable of offering such protection (Nagra 1994a,b) but perturbations to the groundwater (reflecting changes in the regional hydrogeology and hydrogeochemistry) have to be examined (Nagra 1994a). For example, the potential effects of the next ice age could include a very thick permafrost layer which could displace shallow groundwater flow to deeper levels. This could bring younger, less evolved, groundwaters into contact with the EBS, so altering the near-field chemistry. Although it has been shown that such an effect could have a significant radiological impact on a site in the UK (Sumerling 1992), the geothermal gradient in the Swiss crystalline basement is such that it would prevent a permafrost layer getting deep enough to significantly alter flow paths (Nagra 1994b; Thury et al. 1994).

Other potential perturbations considered include the effects of long-term climatic change, increased surface erosion, hydrothermal activity and intrusion of saline groundwaters from the north Switzerland Permo-

Carboniferous Trough into the repository zone. The low hydraulic conductivity of the crystalline basement and the presence of overlying aquifers means that the first two perturbations are extremely unlikely to make significant differences to the EBS, because the deep groundwater flux will remain low and the residence time long enough to ensure significant rock/water interaction to buffer any extremes in groundwater chemistry. The third, hydrothermal effects, can be avoided by careful siting (the probability of any significant activity at an unexpected site is, in any case, very low). In the fourth case, the intrusion of saline waters (maximum total dissolved solids of 13gL^{-1} ; Pearson et al. 1989) into the repository zone, the analysis in the Kristallin-1 report is unclear. If the concern is only about saline water intrusion, then the example of the Swedish and Canadian programmes, where the groundwater at the repository horizon will be saline, indicates no significant problems. However, brines (maximum total dissolved solids of 117gL^{-1} ; Pearson et al. 1989) are also present in the Permo-Carboniferous Trough and if these waters were to intrude into the repository horizon, then the effects could be more significant (the interaction of saline groundwaters and brines with compacted bentonite is currently being studied by SKB in Sweden and PNC in Japan).

Brines could alter the chemistry of the near-field pore fluids but, as noted above, would have little effect on Eh/pH which would remain in the reducing/alkaline range due to buffering by the canister and bentonite. Higher salinity may affect canister or waste form corrosion rates, but there is a sufficiently large empirical database of experimental and natural analogue data to indicate that any increases are unlikely to be large enough to have a significant impact on releases. An increase in salinity could also influence elemental solubility; effects are expected to be relatively small, but the modelling approach used to support the selection of solubility data breaks down at ionic strengths $\sim 0.1\text{M}$. Alternative formalisms are available (eg the Pitzer approach) but appropriate databases are currently lacking. Nevertheless, empirical databases developed by the waste management programmes considering disposal in salt (eg Germany, USA), can be used to support the assumption of no major influences.

The final possible influence of increased salinity is on the transport barrier role of the bentonite. Empirical data indicate that the stability and pore structure (colloid filtration) will not be significantly altered by saline fluids. The retardation of some nuclides will be decreased (eg Muurinen et al. 1985) but would not be expected to fall below the conservative values currently used to assess repository performance.

As noted in the sensitivity analysis above, higher fluxes of water will not cause unacceptable degradation of the EBS performance as long as the barriers are not directly disturbed (releases of radionuclides are low even for a zero concentration boundary at the outer edge of the bentonite, corresponding to an infinitely high water flow).

High flow rates of water could, however, potentially erode the bentonite which, as noted above, is a key component of the EBS. Major water fluxes through the crystalline basement are, however, localised in major fracture zones (Thury et al. 1994) which would be avoided during repository location and construction. The water flux in the smaller fractures and microfractures of the blocks of rock between such fracture zones is much less and has been assessed to be below critical values for erosion to be significant (Nagra, 1994a). This conclusion is supported by extensive rheological studies of compacted bentonite and is currently undergoing laboratory tests in Japan (PNC 1993). Were erosion to be shown to be a problem, it could be alleviated by adding sand to the outer layers of compacted bentonite (Coons et al. 1987).

Relevance for other wastes

When compared to the disposal systems considered for other types of toxic waste, the HLW repository design presented here appears to be completely over-specified. The rationale for this over-design is primarily socio-political – reflecting the concern of the general public about radioactivity and the extremely high value of the product (electricity) relative to the low volume of waste produced for the case of nuclear power. Nevertheless, the principles of defence in depth via a multi-barrier system and robust long-term performance of an engineered barrier system might be taken over to other waste management systems.

It is likely that custom-built, deep geological repositories could not be justified for most chemical/toxic wastes on financial grounds, but many potentially suitable cavities exist as a result of mining activities. For toxic wastes which do not decay, or decay only slowly on a geological timescale, the advantages of being able to isolate the containment system from surface/near-surface perturbations is considerable.

In a dry or low flow environment, very long lifetimes of engineered structures can be assumed if they are chosen to be compatible with the geochemistry of their surroundings. Multiple barriers can provide a low solute transport environment even in the event of localised perturbations of the host rock (eg using plastic clays) while chemistry is buffered in an Eh/pH range conducive to low release of waste components; for many metals, alkaline (pH 8-10), reducing conditions are particularly favourable. The use of micro-porous materials to ensure that a colloid source term does not exist is clearly advantageous.

Barriers will eventually degrade and waste will be released to the accessible environment. The EBS should delay such releases as long as possible for wastes which decay and, for all wastes, spread releases over as long a time period as possible (temporal dilution – e.g. due to low solubilities, sorption, transport resistance).

The geological barrier can provide further delays of release and temporal dilution due to retardation/dispersion processes, of which sorption and matrix diffusion are particularly important. Experience in the radwaste industry has shown, however, that characterisation of the geological barrier in sufficient detail to confidently quantify such processes is particularly challenging. The hydraulic contrast between the host rock and surface aquifers, on the other hand, might be easier to predict with confidence and such dilution might be a valuable component of a safety case. This leads to the rather counter-intuitive conclusion that, for many waste types, although a dry environment (e.g. unsaturated zone in a desert) might have many advantages from the pure safety viewpoint, it may be easier to demonstrate the safety of a wet, low permeability host rock which is overlain by a massive aquifer, as is planned in Switzerland among other countries.

Finally, it is worth noting that the natural analogue approach to building confidence in the long-term behaviour of a repository is of considerable importance in making a clear safety case for radwaste isolation systems. This is slowly being taken up by the chemo-toxic waste industry (see Brassler 1997; Come 1997) and will surely gain pace in the coming years as the regulations for toxic waste disposal almost inevitably become more and more strict.

Conclusions

Although initially designed purely from the engineering viewpoint, the current design of the EBS of the Swiss HLW repository also utilises chemical containment processes to retard releases of radionuclides to the far-field. In most cases, due to the decision to use only well understood materials in a robust design, the chemistry of the system is reasonably well understood. Arguably, the geochemical conditions in the far-field are less well understood, but this is less of a problem so long as the host-rock can be shown to provide the near-field with:

- mechanical protection

- adequately stable geochemical conditions

- sufficiently low groundwater fluxes past the near-field.

When this can be shown to be the case, then the chemical containment in the repository near-field can be seen to depend mainly on the bentonite buffer via:

- the bentonite pore water chemistry ensuring low solubility of radionuclides

- the pore structure of the bentonite filtering out colloids

- low hydraulic conductivity/strong sorption in the bentonite ensuring slow diffusion.

In terms of potential perturbations to the EBS, the greatest effects are those which have an impact on the bentonite. Careful siting of the repository will remove most, such as illitisation due to a high potassium flux, and most others identified to date are unlikely to have a significant impact on repository performance. Some open questions remain on other potential perturbations, the answers to which would increase confidence in the performance of the repository.

These include:

- a better evaluation of chemical profiles in the near-field with the associated development of a comprehensive model of solute transport in the near-field (along with laboratory/natural analogue verification). This will need, among other information, better data on the bentonite/water and canister/bentonite reactions to further assess the role of chemical fronts in the near-field

- further experimental verification of the assumed absence of colloid transport through compressed bentonite

- unambiguous experimental solubility measurements for selected radionuclides under near-field conditions

- fuller assessment of the likelihood of brines accessing the repository horizon. If this appears significant, then further study of the impact of brines on the bentonite buffer would be useful.

- the likely effect of hydrogen production due to canister corrosion: as noted in the text, the effects could be positive (gas build up stopping corrosion) or negative (escaping gas producing channels which disrupt the bentonite structure).

Lastly, it should be emphasised that the current design for the Swiss HLW disposal system is a 'first generation' design, aimed predominately at concept demonstration. Considerable opportunities exist for optimisation / improvement before repository construction in 2050 and ongoing experiments such as ENRESA's FEBEX will allow improvement in the design of the EBS materials and emplacement methodologies.

Although details are not transferable, the concepts and approaches described here may be relevant to other types of highly toxic waste. Such waste constitutes a much longer potential hazard in absolute terms and its management is certainly a much more urgent problem.

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Table 1. *International HLW disposal concepts: examples of typical key contributions to safety*

Key contribution	Country
Far-field:	
• dry (salt)	Germany, Holland
• unsaturated	USA (Yucca Mt)
• low water flow	Canada, Belgium
Near-field:	
• canister longevity	Sweden, Finland
• chemistry	Switzerland, Japan

Table 2. EBS material inventories (crystalline host rock) per waste package

	Vitrified HLW		Spent Fuel
<hr/>			
Tunnel Diameter			
(m)	2.4	3.7	2.4
Waste			
(m ³)	0.15		0.21
(Mg)	0.4		1.9
Steel Canister			
(m ³)	0.9		3.6
(Mg)	6.5		28
Compacted Bentonite			
(m ³)	52.8	21.3	29.1
(Mg)	110	44	61

Table 3. Summary of the main considerations involved in the selection of solubility limits for specific elements.
 The selection procedure is fully documented in (Berner, 1994).

Element	Rationale for setting solubility limits
Cs, Ni	Very high solubility expected in the absence of co-precipitation processes (arbitrary "high" value selected which could be set as 10 M)
Pa, Sn, Tc, Th, U, Zr, Np, Pu	Main constraint on solubility taken to be formation of the metal oxides (or hydroxides); selected solubilities based on evaluation of uncertainties in thermodynamic data, solid phase crystallinity, laboratory measurements and the likely formation of mixed oxides
Pd	Expected to be effectively insoluble but, conservatively, solubility assessed assuming control by Pd(OH) ₂
Se	Assumed to be set by FeSe ₂ although co-precipitation with S might be expected in reality
Am	Assumed to be set by AmOH (CO ₃)
Cm, Ra	Assumed to co-precipitate with chemically similar elements present in much higher quantities (Am and Ba/Sr/Ca, respectively)

Table 4. Solubility limits for safety-relevant elements (derivation described in detail by Berner, 1994) and sorption data for bentonite from Stenhouse (1995).

	Solubility (molar)		Kd (m ³ kg ⁻¹) ¹	
	Realistic	Conservative	Realistic	Conservative
Am	10 ⁻⁵	10 ⁻⁵	5	0.5
Cm	6x10 ⁻⁸	10 ⁻⁵	5	0.5
Cs	high ²	high ²	0.01	0.001
Ni	high ²	high ²	1	0.1
Np	10 ⁻¹⁰	10 ⁻⁸	5	0.5
Pa	10 ⁻¹⁰	10 ⁻⁷	1	0.1
Pd	~10 ⁻¹¹	10 ⁻⁶	1	0.1
Pu	10 ⁻⁸	10 ⁻⁶	5	0.5
Ra	10 ⁻¹⁰	10 ⁻¹⁰	0.01	0.001
Se	10 ⁻⁸	6x10 ⁻⁷	0.005	0.001
Sn	10 ⁻⁵	10 ⁻⁵	1	0.1
Tc	10 ⁻⁷	high ²	0.1	0.05
Th	5x10 ⁻⁹	10 ⁻⁷	5	0.5
U	10 ⁻⁷	7x10 ⁻⁵	5	0.5
Zr	5x10 ⁻⁹	5x10 ⁻⁷	1	0.1

1. in models of solute transport in natural waters, the interactions of the solute with the solid are usually bulked into a simple distribution coefficient Kd (m³kg⁻¹) which, in the simplest form, may be defined as Cr = Kd.Cw where Cw = the solute concentration in the aqueous phase (mol m⁻³) and Cr = the concentration sorbed on the solid phase (mol kg⁻¹). For further information on the measurement of Kd values, see Sibley and Myttenaere (1986) and, for a discussion of the limitations of the concept, see McKinley and Alexander (1992, 1993a,b,1996).

2. 'high' indicates that the solubility is sufficiently large that saturation could significantly alter the porewater chemistry. For modelling purposes, this "unlimited" value could be set to an arbitrary value which is high enough not to be reached during performance assessment calculations (eg 10 M).