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The potential of natural analogues in assessing systems for deep disposal of high-level radioactive waste

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Stockholm, Sweden August 1984

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A list of other reports published in this series during 1984 is attached at the end of this report. Information on KBS technical reports from 1977-1978 (TR 121), 1979 (TR 79-28), 1980 (TR 80-26), 1981 (TR 81-17), 1982 (TR 82-28) and 1983 (TR 83-77) is available through SKB.

THE POTENTIAL OF NATURAL ANALOGUES IN ASSESSING SYSTEMS FOR DEEP DISPOSAL OF HIGH-LEVEL RADIOACTIVE WASTE

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ABSTRACT

Many of the processes which will lead to the breakdown of engineered barriers and the mobilisation of radionuclides in a deep waste repository have analogies in natural geological systems. These "natural analogues" are seen as a particularly important means of validating predictive models, under the broad heading of radionuclide migration, which are used in long-term safety analyses. Their principal value is the opportunitiy they provide to examine processes occuring over geological timescales, hence allowing more confident extrapolation of short timescales experimental data.

This report begins by reviewing the processes leading to breakdown of containment in a high-level radioactive waste repository in crystalline bedrock and the subsequent migration mechanisms for radionuclides back to the biosphere. Nine specific processes are identified as being of the most significance in migration models, based on available sensitivity analyses. These processes are considered separately in detail, reviewing first the mechanisms involved and the most important unknowns then the types of natural analogue which could most usefully provide supporting evidence for the effects of the process. Existing studies are assessed and possibilities considered for additional analogues. Conclusions are drawn, for each process as to the extent to which analogues validate current predictions on scale and effect, longevity of function, etc. Where possible, quantitative evaluations are given, derived from analogue studies.

A summary is provided of the conclusions for each process, and the most important topics for furhter studies are listed. Specific examples of these requisite analogues are given.

The report emphasises throughout the importance of linking analogues to well defined processes, concluding that analogues of complete disposal systems do not exist. While the report is aimed specifically at the Nagra (Switzerland) and KBS (Sweden) concepts for disposal of high-level wastes or spent fuel, the results are seen to be more widely applicable. A considerable amount of the information reviewed and presented could be used in the assessment of disposal of other waste types in other host rocks.

CONTENTS

1. INTRODUCTION

The central issue in assessing the long-term performance and safety of a radioactive waste disposal facility is our ability to predict confidently the nature and effect of processes and geological events far into the future. Assessment models which are deterministic require evidence that processes which they predict will actually occur in the same magnitude and time scale, and probabalistic models require evidence that events will or will not occur, and with what likelihood. It is questionable whether laboratory-based data can be successfully extrapolated over time scales approaching hundreds of thousands of years, especially when bearing in mind the complexity of the reactions and alteration processes which will accompany, for example, the burial of high-level radioactive waste and the subsequent dispersal of radionuclides into a groundwater environment. In attempting to achieve a better understanding of the longterm perspective, the geological and geochemical aspects of radioactive waste disposal may be improved on and tested by examining appropriate analogies represented in the geological record. The strength of analogue studies lies in the opportunity they provide to observe natural geochemical processes which resemble the processes considered important in the containment of radioactive waste over a time-scale and at a level of complexity generally impossible to simulate under laboratory conditions.

The use of natural analogues to gain scientific insight into the behaviour and containment of high-level radioactive waste (HLW) is not new. Some containment concepts and principles, such as the selection of engineered barrier components and emphasis on the role of certain redox and retardation processes, are in fact derived from an understanding of natural systems. For example, the study of hydrothermal and natural radiation effects on clay formations have contributed important information on buffer zone material requirements. Radionuclide mobility and retention in the event of canister corrosion and leakage has attracted considerable attention. This has led to geochemical studies of suitably delineated uranium ore occurrences and their host rocks. Using isotopic methods, such as uranium-series disequilibrium measurements, the behaviour of the isotopes of uranium and their radioactive daughters can be determined within a time-scale encompassing the last million years or more. How naturally-occuring radionuclides move through a rock/groundwater system and how their movement may be restricted are of paramount importance in safety assessment.

The types of natural systems which can be examined are, by virtue of different disposal concepts and waste forms, necessarily wide-ranging and must therefore take into consideration a broad spectrum of geological processes and environments.

This report was, however, conceived principally to relate analogue studies to the KBS (Sweden) and NAGRA (Switzerland) concepts of high-level radioactive waste disposal in a crystalline bedrock repository. However, much of the discussion and many of the conclusions are relevant to other disposal environments. The important geochemical processes described in the report and their possible natural analogues consequently pertain mostly to high-level radioactive waste. Low- and intermediate-level waste forms, and concepts for their disposal have not been considered directly although much of the discussion can be equally relevant to these topics, particularly as regards radionuclide migration. Furthermore, natural analogues of biological uptake and transfer in plants and animals have been excluded. Studies of archaeological artefacts, not initially planned to be included, have received some detailed attention because of their obvious use in the assessment of metal durability within known periods of time.

This report has been written very much with the geologist in mind. The responsibility of finding and assessing the suitability of natural analogue systems must lie with the field geologist and geochemist. By providing what we hope is a logical account of the main geochemical processes involved in assessing the behaviour of deeply buried high-level radioactive waste we hope to bridge the gap between them and the more laboratory-orientated scientific fraternity.

2. PROCESSES AND CONCEPTS REQUIRING TESTING

In order to apply natural analogues to the maximum advantage when testing disposal system performance models it is important to have a clear understanding of all the processes leading to release and migration of radionuclides. The first essential is thus a conceptual model of the disposal system itself.

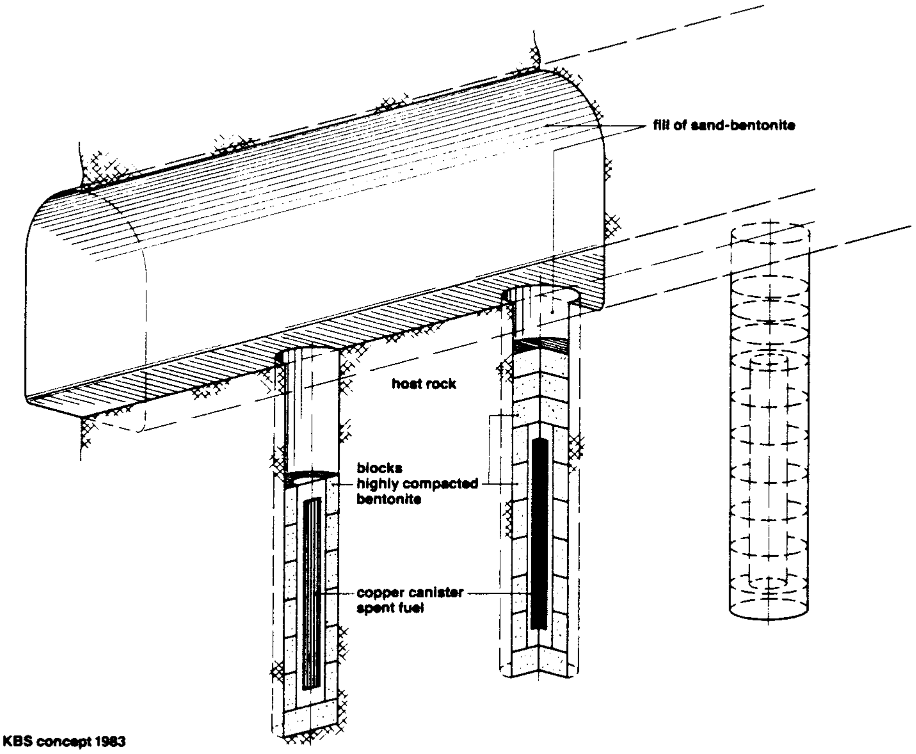
2.1 The NAGRA and KBS concepts for disposal of HLW

The Swiss and Swedish concepts for burial of HLW in crystalline rocks are very similar in underlying rationale and in general engineering terms, although there are some important differences in the design of the engineered barriers.

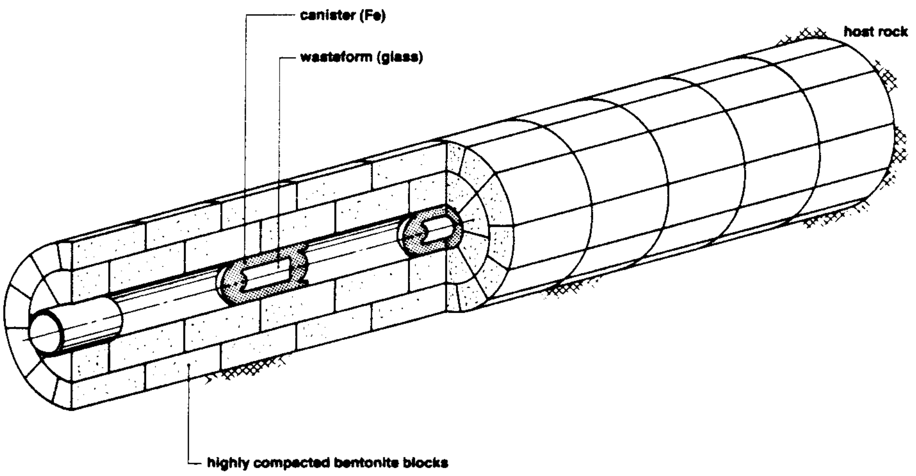
Both concepts involve the excavation of a repository in crystalline basement rocks at a depth of between 400-1000m (KBS) or 1000-1800m (NAGRA), depending on local geology. The NAGRA concept envisages utilising crystalline bedrock which occurs at some hundreds of metres beneath a sequence of younger sedimentary rocks, hence the greater repository depth.

The repository would comprise a series of parallel galleries in which disposal of waste packages would take place. Individual packages would either be emplaced vertically in shallow wide-diameter boreholes spaced at intervals along the gallery floor or situated horizontally along the axis of the gallery at intervals, being emplaced at the same time that the tunnel is being backfilled (see fig. 1). The packages are surrounded by a buffer of highly compacted bentonite clay, which in its "dry" compressed state can be emplaced as machined blocks designed to completely fill the annulus (either borehole or tunnel) between the packages and the rock. In the KBS concept the gallery above the boreholes is backfilled with a mixture of sand and bentonite, compacted in-situ or sprayed into place. As the bentonite buffer and backfill absorb water from the surrounding rock they expand to fill completely all the voids and to form a homogeneous and impermeable barrier between the rock and the waste packages. Both concepts will probably also use bentonite as a major component of the seals which are required during completion of the repository when access shafts are being backfilled and closed.

Figure 1: Schematic illustrations of the KBS (a) and NAGRA (b) system of waste emplacement and engineered barriers.



a) KBS concept 1983



b) NAGRA concept 1984

The waste packages themselves consist of an internal container (canister) of stainless steel holding the high-level waste. The waste might be either vitrified HLW (borosilicate glass) or the actual spent fuel elements themselves. In the latter case the gaps between individual elements may be filled with either lead or copper, meaning that the spent fuel container is essentially solid metal. In the spent fuel disposal concepts the container is also made of thick copper rather than steel, and no outer overpack is envisaged. For vitrified HLW the steel container holding the glass will be surrounded by a thick overpack to complete the package. This may be either thick copper (KBS) or very thick cast iron (NAGRA).

The principal differences between the two designs are thus in the nature (and functional role) of the outer package material (essentially thick copper or thick cast iron) and in the thickness of the clay buffer between the packages and the rock. In most other respects the concepts can be treated similarly (function and performance of barriers, geological behaviour, etc.). More detailed descriptions of the Swiss and Swedish proposals are given by KBS (1978; 1983) and NAGRA (1983).

2.2 Mobilisation and transport reveiwed

Mobilisation and transport are inevitable consequences of geological evolution within the repository. We now endeavour to break this complex evolution down into a number of inter-related machanisms or processes which can be assessed reasonably independently. The objective is to assign natural analogues to each of these processes. The relative importance of the processes is discussed in the next chapter. First it is necessary to review the complete mobilisation and transport sequence in a general sense, applicable to both the NAGRA and KBS disposal concepts outlined in the previous section.

This description starts at the point where the waste packages, surrounded by their bentonite buffer, have been completely isolated and the disposal galleries backfilled and sealed. The reference scenario will then proceed as follows:

1. Water re-invades zones of the repository host rock which have been partially drained during operation. The hydrogeological environment begins to stabilise, and the bentonite buffer begins to absorb water and swell.

2. At the same time the radiogenic heat from the waste begins to spread through the buffer and into the host rock. Temperatures in the near-field reach a maximum within a few years to a few decades after disposal (depending on concept).

3. Within the same time period the bentonite becomes saturated and exerts a swelling pressure on the surrounding rock and the waste packages, sealing any remaining "construction gaps" in the backfill structure.

4. Warm clay porewaters come into contact with the canister overpack and a process of corrosion begins, controlled by the rate at which groundwater or corroding species can diffuse from the rock through the clay to the package surface. The rate of removal of soluble or gaseous corrosion products and the build-up of reaction layers also affects the corrosion rate.

5. At some point container failure occurs as corrosion eats through the overpack and canister, possibly enhanced by localised pitting. Failure may occur by corrosive penetration or as a result of mechanical weakening of the package caused by corrosion. In the case of spent fuel disposal the lead or copper matrix surrounding the waste must also be dissolved before water can contact the waste. The time to first access of water to waste will generally be very long and certainly occur after the heat emission of the waste has declined to insignificant levels. Depending on concepts, conservative estimates range from about 1000 to more than 10^5 years. However, it is occasionally assumed for safety analyses that some if not all containers may corrode through within about 100 years. This is unjustifiably pessimistic from the design point of view but may be a useful limit for safety analyses.

6. When water eventually contacts the waste, the near-field will be comprised of host rock which has undergone very mild hydrothermal alteration, an intact clay buffer, and a mass of poorly soluble overpack and canister corrosion products, plus uncorroded container materials. Near-field transport processes will still be controlled almost entirely by the bentonite. The thermal, mechanical and chemical stability of this component is thus central to the system performance.

7. Waste-form dissolution will proceed in the same manner as container corrosion, with slow leaching and mobilisation of radionuclides. In spent fuel solid state diffusion may be an important release mechanism (albeit very slow) for some elements, but in addition rapid release of unbound species ("prompt" iodine accumulated around fuel element edges for example) can occur. In the unlikely event of canister breaching within the early thermal period such that hot leaching can occur, the possibility exists of forming waste-containing hydrothermal mineral phases from (for example) glass corrosion products. Such a secondary mineralogy will develop at any temperature as a result of rock-waste-water interaction, but its role as a retardation machanism will be most pronounced at higher temperatures.

8. The speciation of mobilised radionuclides will depend on the complexing ligands present in the porewater, the pH and the redox conditions. Owing to the very small pore-size and great tortuosity of the bentonite it is extremely unlikely that colloidal species (homogeneous radiocolloids or radionuclides sorbed onto natural colloids) will diffuse out to the buffer-rock boundary; only dissolved species are likely to migrate this far. Redox conditions have a great influence on the solubility of some radionuclides and will be buffered by the container material and its corrosion products and could be affected by radiolysis of the porewaters. Owing to radiolysis, conditions around the waste are in fact generally considered to be oxidising with a possibly abrupt change to reducing conditions (redox front) caused by buffering either by the iron overpack (Fe/FeO) or iron oxides (e.g. magnetite) present in the backfill or host rock.

9. The redox front may move out into the rock very slowly as the iron buffering capacity is progressively exhausted, but this will take a considerable time. During this period radionuclides will have diffused out to the rock at very low concentration controlled either by their solubilities or by their slow release from the waste matrix and the redox sensitive elements may precipitate at the redox front, to be picked up and moved along in a typical "roll-front". Others may be co-precipitated or may be free to migrate in the mobile groundwaters either in solution or, now, as or on colloids. The whole of this process is generally estimated to be restricted to the container itself, or to within a few metres of the containers for at least 10^5 - 10^6 years, and consequently only radionuclides with long half-lives are involved.

10. Far-field transport will take place by groundwater flow in a limited number of significant fractures arranged in an interconnected network in the rock. These fractures will have higher conductivities than the other more numerous fissures, and very much higher conductivities than the intact rock mass. The majority of these "flowing" fractures will have zones of alteration around them characterised by gradational porosity profiles and alteration minerals.

11. Radionuclides will be transported through the fractures at a velocity less than that of groundwater due to physico-chemical retardation. Various mechanisms are involved including physical (van der Waals) adsorption, ion-exchange, ultra-filtration, ion-exclusion and chemisorption (reversible or irreversible). Such retardation, often loosely termed "sorption" in the following text, will vary greatly between radionuclides, being very small for anionic species (e.g. I) and so large for some complexed cations (e.g. Pu, Th) that they can be considered as totally immobile in some geological environments.

12. In addition to sorption and radioactive decay, the radionuclide concentration and peak arrival time at the biosphere will be controlled by dilution and physical dispersion as progressively more and more of the fracture network is invaded by the leachate. This effectively "dilutes and delays". In addition radionuclides will diffuse out of the fracture-bound water into static porewaters in the enhanced porosity zones and possibly even the intact rock. Only when the concentration gradient is reversed can any net movement back out into the flow system take place. This is thus thought to be an effective delay machanism for unsorbed radionuclides as well as making available a larger rock surface area for sorption. This process is commonly known as matrix diffusion.

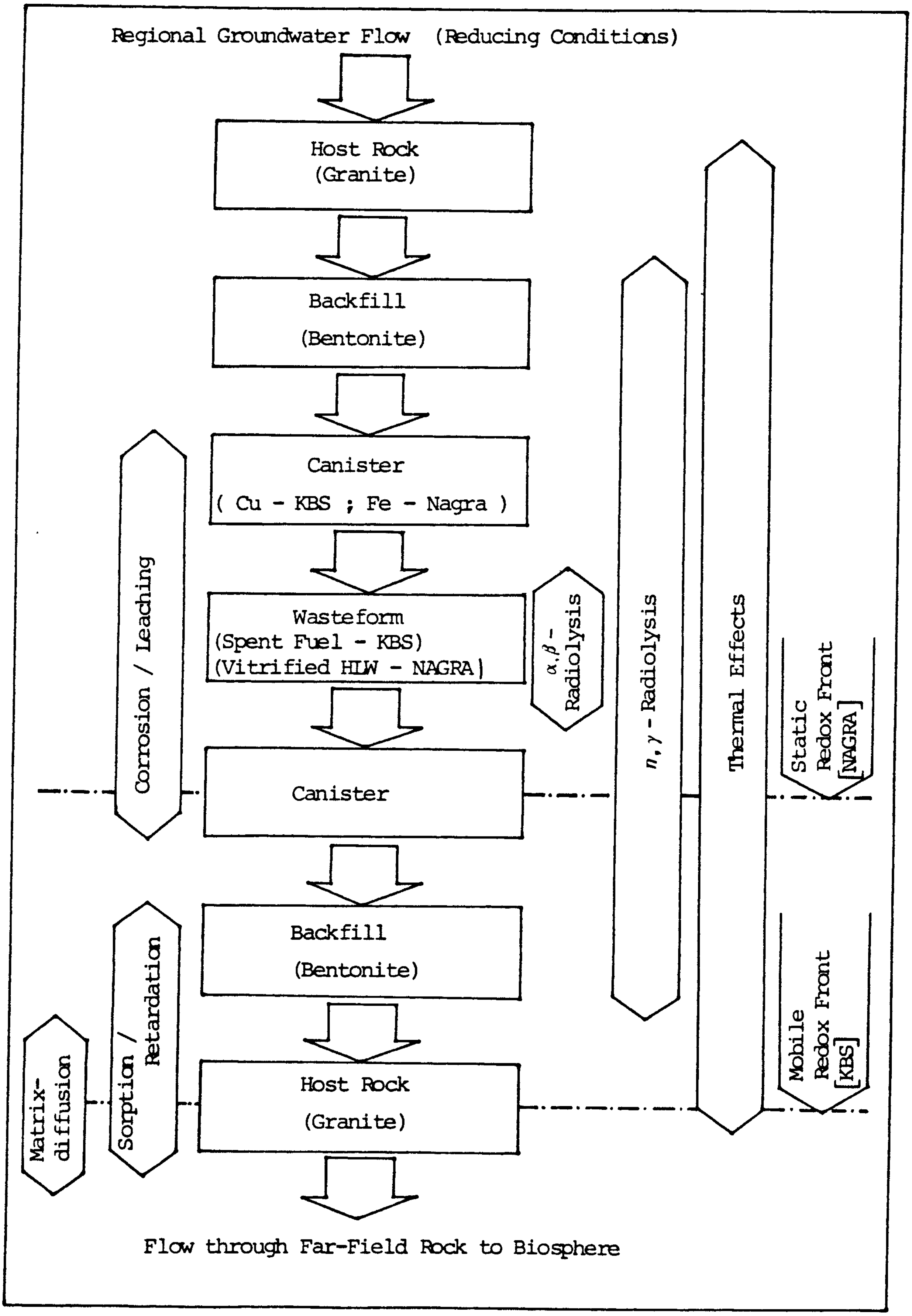
13. Release is generally assumed to take place when the fissure waters reach the biosphere at springs and water wells, or via lakes, streams, aquifers and the sea. The biological uptake processes, although amenable to natural analogue studies, are not included in this report. Interested readers are referred to Drew and Eisenbud (1966) and Eisenbud and Franca (1984) for examples of natural analogue approaches to uptake based on the Morro do Ferro thorium deposits in Brazil.

The mechanisms and evolutionary process described above are shown schematically in Figure 2. For the purposes of simple assessment of analogues we have selected nine key processes which cover all the important aspects of disposal system performance. These are:

1. Thermal/chemical breakdown of buffer and seal materials (principally bentonite).
2. Waste package corrosion.
3. Waste-form dissolution and breakdown.
4. Solubility and speciation of radionuclides.
5. High-temperature mineralogical fixation.
6. Radiolysis.
7. Redox equilibration.
8. Retardation during transport.
9. Matrix diffusion.

In the following sections the relative importance of these nine processes is discussed, and available and potential analogues assigned to each.

Figure 2: Flow Diagram of Radionuclide Release from HLW



3. RELATING ANALOGUES TO PROCESSES AND ASSESSING THEIR COMPARATIVE SIGNIFICANCE

3.1 How natural analogues work

To be useful a natural analogue must be tightly constrained to some particular process, with the boundary conditions well defined. Analogues of a complete disposal system do not exist, since even in the case of the nearest approach (fossil reactors) the boundary conditions are significantly different or unknown. Such analogues cannot be used as a large-scale and wide-ranging control on a rigorously modelled dose calculation. In order to provide either validation or benchmarks the analogue must be tied to a particular process, or combination of processes, critical to the overall model.

The important processes in a full system performance assessment were outlined in the previous chapter. The rôle of a natural analogue should be to confirm:

a) that the process is in fact something which can or will occur in practice as well as in theory, and in nature as well as in the laboratory

b) where, when, and under what conditions it can occur

c) that the effects of the process are those envisaged in the model

d) that the magnitude of the effects in terms of physical scale and time are similar to those predicted for a similar set of conditions.

All of the processes outlined earlier are essentially chemical or physico-chemical in nature, and consequently the analogues to seek lie in natural geochemical systems.

The requisite conditions are most commonly encountered in ore deposits (either pre-existing or in the process of formation) and not surprisingly these provide the most accessible and useful analogues for a number of the processes outlined above. However, any system where a geochemical anomaly exists, implying lack of equilibrium, can be useful. Thus the contact between two bodies of rock of dissimilar composition, or the interaction of porewaters or groundwaters with a rock or mineral can provide good analogues. The essentials to bear in mind when selecting analogues are as follows:

- The process involved should be clear-cut. Other processes which may have been involved in the geochemical system should be identifiable and amenable to quantitative assessment as well, so that their effects can be "subtracted"

- The chemical analogy should be good. It is not always possible to study the behaviour of a mineral system, chemical element or isotope identical to that whose behaviour requires assessing. The limitations of this (discussed in Chapter 4) should be fully understood

- The magnitude of the various physico-chemical parameters involved (P, T, pH, Eh, concentration, etc.) should be determinable, preferably by independant means and should not differ greatly from those envisaged in the disposal system

- The boundaries of the system should be identifiable (whether it is open or closed, and consequently how much material has been involved in the process being studied)

- The timescale of the process must be measurable, since this factor is of the greatest significance (the raison d'être) for a natural analogue.

Whether an analogue can be applied quantitatively (as an actual control or benchmark on a model), or only qualitatively (as a "sign-post" that the model is going the right way) will be strongly dependent on how many of these conditions are satisfied, and with what degree of confidence.

In all cases there will be some limitations owing to inability to define adequately all these conditions. Some important processes appear not to be amenable to natural analogue control. These are generally physical processes which are site-specific; groundwater flow for example. The only analogue for the study of one flow system is the study of another in a similar environment. Processes not correlated by analogues are thus those which, to be studied, must be observed on the same "real time" scale as that of the process. These processes are, however, few, and certainly in the chemical field there are no processes or situations for which some of the conditions specified above cannot be satisfied: enough that is to give at least a qualitative assessment.

3.2 Relative significance of the processes in system assessment

At present complete systems analyses, assessed for sensitivity to parameters and their co-variance, have not been carried out by KBS or Nagra. Two approaches have been used instead to assess repository performance, both of which include large degrees of technical conservatism. KBS-3 calculated releases for a single pessimistic model where various retardation processes were attributed little or no containment rôle, and a number of pessimistic assumptions were made on events which might lead to accelerated releases. Essentially the model looked at a waste containerbuffer system, linked at the outflow side to a 100 m long fracture system in the rock along which all flow took place until a major vertical fracture from the surface is encountered. This point, where dilution occurs in fracture-bound waters, is taken to be the interface with the biosphere. Variants on this scenario included the assumption of oxidising conditions, of preferential colloid transport, and of breach of the waste containers after 100 years (the copper container being attributed a lifetime of 10^5 - 10^6 years for the other scenarios).

Current safety assessment studies at Nagra are adopting a somewhat different approach. Realistic migration pathlengths (greater than 2km) are assumed for migration from a repository at 1300 m depth in granite below sediments to an outflow point in the fluvial sediments of a major river. Various retarding processes are either varied in the magnitude of their influence, or attributed zero value. Both the Nagra and KBS studies use realistic groundwater flow velocities and volumes within the near and far fields, although the KBS far field comprises only 100 m of rock. In many aspects, owing to the difference in approach, the two assessments cannot be easily compared, and it is difficult, using available information, to attribute relative degrees of importance to the processes included in the models. While some processes (such as matrix diffusion, dilution on release, and the propagation of oxidising conditions into the rock) stand out as being extremely significant to calculated doses, the role of others cannot be determined without a sensitivity analysis.

3.2.1 Sensitivity and co-variance analysis

Much has been written recently on the relative importance of particular parts of the multi-barrier system in controlling eventual doses to man. The rôle envisaged for each part of the containment system, and the predicted performance of each system element, varies from concept to concept. A rigorous sensitivity analysis of the complete release-migration-uptake process uses performance parameters for each component which are varied to bracket completely the worst to the best possible behaviour of these components. In the extreme each barrier can be attributed, in turn or in combinations, no functional rôle, and the effect on doses assessed accordingly. In this way the relative influence of each of the processes outlined in the previous chapter on eventual calculated doses can be assessed. Some processes, or some specific aspects of the behaviour of a particular part of the disposal system will be found to be much more important than others.

A generic review of several such analyses (for HLW disposal in salt, basalt, and granite host rocks) is reported by Burkholder (1983). Although limited in scope, this makes a useful starting point for assessing which features of a disposal system may most require the benchmarking provided by natural analogues.

The principal conclusions of the section of Burkholder's review concerning disposal in granite were that:

a) waste containers with lifetimes longer than 0-100 years are unnecessary

b) seeking to achieve transport rates of any of the radionuclides out of the engineered barriers which were lower than 0.01 % of the initial inventory each year is not justified. This rate was called the "man-made subsystem transport rate", and the conclusion can be restated as follows. Even if all the waste is mobilised and enters the final (geological) barrier only 10,000 years after burial, eventual doses will be little different from those which would arise assuming very much longer term dissolution rates.

Burkholder concludes:

> "The simplified approach to the evaluation reported here is not likely to be sufficient for the performance assessment of a specific isolation system because it does not explicitly consider all potentially relevant phenomena and all their potentially complex system-specific interactions. Furthermore, it treats the uncertainties in our understanding of the effects of isolation system phenomena by conservative use of models and data rather than by performing an uncertainty analysis. However, overall geologic isolation system performance is so robustly insensitive to the time that radionuclides first begin to move away from the waste form that the possibility of a more detailed, system- specific analysis reversing the conclusions regarding container lifetime seems remote. Likewise, the large conservatisms inherent in the literature studies upon which this evaluation is based and the wide range of parameters investigated make it unlikely that system-specific analyses will weaken the conclusions regarding the man-made subsystem transport rate. Thus, the use of waste containers with long lifetimes and man-made subsystems with very low transport rates seems unjustified from a technical standpoint and a geologic isolation point of view."

The conclusions of this work are founded largely on the apparent massive retardation effect of the final geological barrier during migration. Even very short groundwater transport times (approx. 500 years) and sorption coefficients an order of magnitude lower than those commonly considered appropriate, do not affect the conclusions. On this basis then, the principal requirement for natural analogues is in the areas of chemical and physical retardation processes in the geosphere (areas 8 and 9 from the list at the end of chapter 2).

However, Burkholder's approach examines only two of the rôles of the engineered barriers; delaying the initiation of releases, and retarding migration prior to entry of radionuclides into the host rock. Both the Nagra and KBS concepts allocate other rôles to the container and clay buffer which effect two other important processes: the rate of release of radionuclides from the waste form, and their speciation in solution.

In the Nagra concept using a thick iron container (with a limited lifetime to breaching, around 1000 - 10,000 years) the canister corrosion products act as a redox buffer to ensure that any radiolytic oxidation front remains within the engineered barriers for at least one million years. Both concepts require that the transport of water or corrodants to the container, and the availability of "fresh" groundwaters to attack the waste are limited by the hydraulic properties (essentially zero flow, diffusional transport only) of the clay buffer, which may also act as a barrier to colloid transport.

Thus while the lifetime of a container (in terms of its acting as a barrier to water access to the waste) and the retardation rôle of the buffer appear in one analysis to be relatively unimportant, we are still interested in area 2, the lifetime of the container as a chemical buffer (Nagra) and area 1, the preservation of hydraulic properties of the clay buffer to minimise waste mobilisation rates (KBS and Nagra).

Burkholder's analysis does not take account of various processes which have recently been identified as important (e.g. colloid transport, redox fronts) but nonetheless provides a reasonable basis until such time as updated sensitivity analyses for the KBS and Nagra concepts come available. Such analyses would resolve differences between the concepts (principally that of container type and lifetime). In a separate study of the environmental impact of actinides from spent fuel emplaced in fractured rock with an inconfined water-table, Brotzen (1983), concludes that the key processes are the attainment of reducing conditions during groundwater transport and the bypassing of the repository by a major part of the total groundwater flow through the bedrock. This is based on common spacial distributions of hydroconductivities combined with generalized geochemical analogues as well as supplementary laboratory data, indicating reductive precipitation of uranium and coprecipitation of the toxic actinides. The time for radioactive decay provided by the canister buffer zone and hostrock are not of critical importance in this model. At present therefore different views exist on the significance of the separate processes and factors. However, from available data it seems possible to rank the processes into order of importance in the following broad groupings:

1. Retardation mechanisms in the geosphere (areas 8 and 9)

2. Speciation of radionuclides (areas 4, 6, and 7)

3. Buffer performance and longevity (area 1)

4. Waste form breakdown and canister corrosion (areas 2 and 3)

5. High temperature element fixation (Area 5).

The significance of the last two groups of processes is probably considerably less than the first three.

4. NATURAL ANALOGUE SYSTEMS

Within the various geological disciplines there already exists a wealth of information accumulated over the years on different geological environments, geochemical processes and experimentally-related studies, which have not yet been applied directly to the problem of radioactive waste disposal. As outlined in a pre-conference circular (GSA Penrose Conference on "The Geochemistry of the Environment Near a High-Level Nuclear Waste Repository"):

> "The available geological information includes field studies of lowgrade metamorphic rocks and fluids, reactions and transport mechanisms for hydrothermal ore deposits, clay stability, metallic corrosion in a geological environment, water migration in a thermal field, solution chemistry effects (i.e. pH, Eh, complexants) on mineral phase stability - particularly radionuclide-bearing phases, experimental determination of sorption and solubilities of radionuclides under geological conditions, and the formation of colloids as a potential nuclide transport mechanism."

This list can be extended by including hydrogeological characterisation of crystalline bedrock environments, alteration mechanisms of crystalline rocks under ambient temperatures, natural glass and mineral stabilities in relation to solidified waste forms, and many others. There are, therefore, many geoscientists who are actively engaged in geologically-related areas who, given the necessary stimulation and support, could apply their expertise to the problems of nuclear waste isolation. This is discussed further in Chapter 6.

Some application of existing geological information, combined with supplementary data, has already been directly related to the problems of high-level radioactive waste disposal in crystalline rock environments. Within the last three years, Australia, Canada, Sweden, U.K. and U.S.A. have conducted limited programmes of natural analogue feasibility studies; programmes in France and Switzerland are presently being initiated. An assessment of the success of these studies can already be made, and this is outlined in Chapter 5.

4.1 Some Chemical Considerations for Natural Analogue Studies

The nine geochemical processes (Chapter 2) represent an initial interaction of groundwater with the engineered barriers (bentonite buffer; canister), the release of radionuclides as the canister is breached, and then the interaction of the released radionuclides under a variable set of physico-chemical parameters particular to each barrier form (engineered and otherwise), as it is being penetrated. A thorough knowledge of how the important radionuclides behave within a wide range of physico-chemical conditions, and their analytical measurement, is thus an important pre-requisite for natural analogue studies.

Only a small number of the radionuclides initially present in high-level nuclear waste are identified as being of importance for repository safety analysis (e.g. KBS, 1983; Hadermann and Rösel, 1984). These nuclides either have sufficiently long half-lives to survive in significant concentrations for the long times required for penetration of the engineered and geological barriers, or are the radioactive daughters of such species (Table I). An extensive body of laboratory geochemical data has been compiled for these elements including speciation and solubility (e.g. Allard, 1983; Schweingruber, 1983), sorption data (e.g. Allard, 1982, Allard et al, 1983b; Andersson and Allard, 1983; McKinley and Hadermann, 1984) and diffusivities (e.g. Neretnieks, 1982; Torstenfelt et al, 1982a). Unfortunately most of these radionuclides are not found at measurable concentrations in relevant geological formations and thus chemical analogues must be used to assess the applicability of such laboratory data to the natural environment over geological time-scales.

4.1.1 The Chemical Analogue

Apart from the natural uranium and thorium series radionuclides the most significant long-lived radionuclides present in HLW (for example technetium, neptunium, iodine, plutonium, americium and curium) are not normally present in measurable concentrations in relevant natural geological systems. However technetium-99 and iodine-129, which occur as natural fission products, and the actinides neptunium-237 and plutonium-239, do exist naturally but only in very small quantities, so that even in and around high-grade uranium deposits, extremely sophisticated analytical procedures are required for their detection and measurement.

TABLE 1: SOME IMPORTANT RADIONUCLIDES IN HLW

ELEMENT	Isotopes of Interest	Half-life (years)
C	14	5.7×10^{3}
Ca	41	1.3×10^{5}
Ni	59	8.0×10^{4}
Se	79	6.5×10^{4}
Zr	93	1.5×10^{6}
Mo	93	3.5×10^{3}
Tc	99	2.1×10^{5}
Pd	107	6.5×10^{6}
Sn	126	1.0×10^{5}
I	129	1.6×10^{7}
Cs	135	2.3×10^{6}
Ra	226	1.6×10^{3}
Th	229, 230	7.3×10^{3}, 7.5×10^{4}
Pa	231	3.3×10^{4}
U	233, 234, 235, 236, 238	1.6×10^{5}, 2.4×10^{5} 7.0×10^{8}, 2.3×10^{7} 4.5×10^{9}
Np	237	2.1×10^{6}
Pu	239, 242	2.4×10^{4}, 3.8×10^{5}

Therefore, in order to study the behaviour of these critical long-lived radionuclides, suitable chemical analogues are required which exhibit similar physico-chemical properties. Such properties include:

- Similar valence state (redox behaviour).
- Similar complex formation (e.g. with OH^-, F^-, $CO_3{}^{2-}$ etc.).
- Similar type of species (i.e. similar stochiometry).
- Comparable ionic radius.
- Half-life long enough to ensure comparable kinetic and chemical behaviour (where different isotopes of the same element are being used as analogues).

Based on these properties, possible chemical analogues for the long-lived radionuclides present in spent nuclear fuel are listed in Tables 2 and 3 (B. Allard, personal communication, 1984). The listed data show the potential use of uranium (depending on its oxidation state) as a chemical analogue for neptunium and plutonium and to a lesser extent protactinium. Thorium has potential use in highlighting the behaviour of protactinium, neptunium and plutonium. The majority of lanthanides correlate closely with americium and curium, whilst neodymium is considered the best analogue for Pu (III).

From Table 2, it can be seen that the importance of uranium as a chemical analogue is considerable. It is therefore fortuitous that uranium is one of the most common and abundant of the naturally-occurring radionuclides, being present in at least minute quantities in all rock-types and in natural groundwaters. Because of its economic importance as a nuclear fuel and its characteristic physico-chemical and isotopic properties, the geochemical and hydrochemical behaviour of uranium within most bedrock environments has been studied in detail and is well-documented in the published literature. In contrast, because of its general geochemical and hydrochemical stability and low economic importance, the available data on thorium are less extensive. There is some debate about the suitability of thorium (existing only as Th IV) as a chemical analogue of plutonium (III, IV and V oxidation states). This has been discussed by, amongst others, Eisenbud at al (1984). However, in the absence of a more suitable chemical analogue, any indication of how plutonium might behave under natural conditions should be considered an advantage.

The content and distribution of lanthanides in rocks and minerals has received increasing attention during the last 10 years. Because of their chemical stabilities during long-term geological processes, they have been used to classify the origins and evolution (using chondrite-normalised REE patterns) and date (Nd-Sm ratios) various rock-types and minerals.

The attention received by these analogue elements within the geosciences has meant that the analytical precision and accuracy of their measurement has reached a high level of competence and sophistication. This lends further confidence for their potential use in the reliability of natural analogue studies.

4.1.2 The Natural Analogue

Having established the suitable chemical analogue elements, and defined the key geochemical processes to be investigated, the next stage is to select the best natural analogue system available for study. Some possible combinations are listed below and have already been studied. These are dealt with more fully under Chapter 5. Others offer potential as analogues but have been the subject of only limited work. Their potential is elaborated in Chapter 6.

1. Thermal/chemical stability of the buffer and seal materials

   - Low temperature analogues ($< 100^{o}C$).
     Well defined (T and P) studies of diagenesis and low-grade (greenschist facies) metamorphism of thick sedimentary sequences.

   - High temperature analogues ($> 100^{o}C$).
     Igneous intrusive activity into clay formations.

2. Waste Package Corrosion

   - Geological analogues.
     Stability of native metals in rock samples collected from different rock types and representing both oxidising and reducing environments.
     Stability of iron oxy-hydroxides (e.g. magnetite) in different geological environments.

   - Archaeological analogues.
     Stability of metal artefacts located in surface and near-surface environments.

3. Waste-form Dissolution and Breakdown

- Uranium oxide waste analogues.
  Naturally-occurring uraninite.
- Vitrified/crystalline waste analogues.
  Naturally-occurring volcanic glasses.
  Naturally-occurring minerals (e.g. zirconolite, hollandite, monazite, perovskite, hercynite, etc.).

4. Solubility and Speciation of Radionuclides

- Well-defined geological, geochemical and hydrochemical characterisation of uranium (+/- Th and REE) ore deposits and mill-tailings located in both oxidising and reducing environments.
- Extensive site-specific analysis of natural series radionuclides and relevant elements in groundwaters.

5. High-Temperature Mineralogical Fixation

- High-temperature analogues ($> 300^oC$).
  Contact metamorphic reactions resulting from igneous intrusions into various rock-types representative of the envisaged repository bedrock (i.e. granite, volcanic tuff, salt, etc.).
- Medium-temperature analogues (100-300^{o}C).
  Hydrothermal activity along zones of weakness and fractures in various rock-types. Most useful if hydrothermal solutions have been uraniferous in character.
- Low-temperature analogues ($< 100^oC$).
  Mostly confined to weathering effects at ambient temperatures and preferably under reducing conditions.

6. Radiolysis

- Confined to high-grade uranium ore deposits, particularly where natural nuclear reactors have reached criticality, i.e. Oklo.
- Redox "spots" in slates thought to be due to radiolysis around detrital zircon grains.

7. Redox Equilibrium

- Well-defined geological, geochemical and hydrochemical uranium (+/- Th + REE) ore deposits located up-flow from the groundwater redox front (e.g. sandstone roll-type uranium deposits).
- Availability of Fe^{II} in granitic rocks for oxidation during weathering; the depth of penetration of oxidising groundwaters can be assessed using profiles through weathered crystalline rock terrains.

8. Retardation during Transport in the Far-Field

- Migration analogues.
  Evaluated from concentration profiles (or steady-state radioisotope ratios) resulting from transport from a well-defined source in a known hydrological regime. Possible sources include natural reactor zones, ore bodies, natural series disequilibria in aquifers, chemical discontinuities in sediments and anthropogenic releases (from nuclear weapon tests or the nuclear industry).
- Uptake analogues.
  Steady state elemental concentrations in solution and "sorbed" phases measured. Chemically well-defined elemental sources are required and may be found amongst the possibilities previously considered for migration. Additional consideration of relatively short-lived radionuclides arising from the natural decay series yields data on uptake kinetics.

9. Matrix Diffusion

- Active case.
  Requires ore samples representing a diffusion profile from the edge of a water-conducting fracture surface out into a host crystalline rock. To test the general hypothesis of matrix diffusion, any element source circulated at ambient (KBS, NAGRA) or higher (active hydrothermal systems in line with the U.S. concept) temperatures should suffice. However, because of obvious reasons, circulating natural radionuclides such as uranium are of more direct interest.
- Fossil case.
  Hydrothermal vein deposits (preferably uraniferous). Sampled similarly to the active case above.

TABLE 2 Possible Chemical Analogues for the Long-Lived Nuclides Present in HLW

Element	Oxidation State in Nature2)	Ionic Radius1) (Å)	Hydrolysis Coefficient3) (log K1)	Possible Chemical Analogue
Tc	Red. IV (0)			Re (IV) ?
	Ox. VII	0,64	---	Re (VII) ?
Pa	Red. V			(Th, U (IV))4)
	Ox. V	0,78	9,5	
U	Red. IV	0,76	13,4	U (IV), (Th, Zr. Hf)
	Ox. VI	0,73	8,2	U (VI)
Np	Red. IV	0,87	12,5	U (IV), (Th, Zr, Hf)
	Ox V	0,75	5 1	U (VI)
Pu	Red. III	1,00	6,5	Lanthanides5)
	IV	0,86	13,5	U (IV), (Th, Zr, Hf)
	Ox. IV	0,86	13,5	U (IV), (Th, Zr, Hf)
	V	0,74	4,3	U (VI)6)
Th	Red. IV			
	Ox. IV	0,94	10,8	Th
Am	Red. III			
	Ox. III	0,98	6,5	Lanthanides
Cm	Red. III			
	Ox. III	0,97	(6,5)	Lanthanides

Other important radionuclides (e g I, Cs Pd etc.) have naturally occuring stable isotopes which can be used as direct analogues

1) For the 6 co-ordination state, various values are cited in the literature.

2) Reducing: Eh derived from Fe (II)/Fe(III)
Oxidising: Eh derived from O_2

3) For $M^{n+} + OH^{-} = M\ (OH)^{n-1}$; various values are cited in the literature.

4) The chemistry of Pa (V) is more similar to the 4 valency actinides than the chemistry of the 5 valency actinides (U, Np, Pu).

5) Lathanides - best analogue is Nd
- acceptable Ce Pr, Sm, Eu, Gd, Tb, Dy, Ho
- less acceptable are La (too large), Er, Tm, Yb, Lu (too small); Y.

6) There are no suitable analogues for 5-valency actinides. The best analogue would appear to be U(VI) in the presence of carbonate and at a pH greater than 6-7.

* Elements underlined are those considered most suitable for chemical analogues.

TABLE 3: The Physico-Chemical Characteristics of Potential Chemical Analogues for Long-Lived Actinides Present in HLW

Element	Oxidation State in Nature	Ionic Radius 1) (Å)	Hydrolysis Coefficient 2) (log K1)
Sc	III	0,73	9,7
Y	III	0,89	6,3
(La	III	1.06	5,5
(Ce	III	1,03	5,7
L (Pr	III	1,01	5,9
A (Nd	III	1,00	6,0
N (Sm	III	0,96	6,1
T (Eu	III	0,88	6,2
H (Gd	III	0,94	6,0
A (Tb	III	0,92	6,1
N (Dy	III	0,91	6,0
I (Ho	III	0,89	6,0
D (Er	III	0,88	6,1
E (Tm	III	0,87	6,3
S (Yb	III	0,86	6,3
(Lu	III	0,85	6,4
Ti	IV	0,61	
Zr	IV	0,72	14,3
Hf	IV	0,71	13,8
V	V 3)	0,54	
Nb	V	0,64	
Ta	V	0,64	
Re	VII 3)	0,63	

1) For the 6 co-ordination state, various values are cited in the literature

2) For $M^{n+} + OH^{-} = M(OH)^{n-1}$

3) Other oxidation states probably also occur.

5. APPLICATION OF AVAILABLE NATURAL ANALOGUE STUDIES

The number of geological localities or phenomena which have been studied specifically with the intention of providing analogues for waste disposal is limited. This chapter reviews those which have been studied, before continuing in Chapter 6 to assess which other geochemical data could be used to further the use of analogues.

A wide review of the literature identified a number of general studies or specific analyses of geological features which could be allocated to the nine major processes of interest identified in Chapter 2. These are outlined in Table 4. It can be seen that several of the analogues cover more than one process and consequently can link together to various extents mechanisms of release and migration. In the approach adopted here we have endeavoured to simplify the analogues by examining specifically how they can be used for each individual process. The following nine sections describe the analogues already available for these processes, and assess the limitations or applicability of the available information, specifically with respect to the Nagra and KBS concepts.

5.1 Long-term stability of buffers and seals

The principal role of the clay buffer around the waste packages is to minimise chemical transport rates between groundwaters in the rock and the packages, and vice-versa. When used elsewhere as backfills and seals their main function is as an impermeable flow barrier and generally to provide thermal and mechanical continuity to the rock. Apart from bentonite clay, other materials may eventually be used locally as seals in shafts or boreholes (cements, pozzolans, bitumen, boulder clays, etc.) but since their use has not yet been firmly proposed and as they would in any case be minor constituents of the overall backfill/ seal system, they are not considered in detail here.

Returning to the clay buffer as a transport retardant, it is generally assumed that it would only fulfil this role as it re-saturates with water. The initial blocks of highly compacted bentonite will take up water from the fissure in the surrounding rock, and expand into any remaining voids. In expanding against the rock and waste packages they will exert a swelling pressure of some tens of MPa.

Table 4: The major geochemical processes (1-9) and some related natural analogue systems

Natural analogue	1	2	3	4	5	6	7	8	9
Brusewitz et al. (1974); Brookins (1980); Pusch (1983); ENEA (1982)									
1. Clay: in and around uranium deposits	x							x	
2. Clay: dyke intrusion (Orciatico, Italy)	x								
3. Clay: overlying tuff (Orte)				x			x	x	
4. Clay: underlying a volcanic sill	x								
5. Clay: fracture fillings in crystal. rocks	x								
Johnson and Francis (1980); Bresle et al. (1983)									
1. Archaeological studies		x							
2. Native metal studies		x							
Ewing (1979); Zielinski (1979, 1980); Kaplan (1980); Lindqvist and Latikari (1980); Malow and Ewing (1981); Ericson (1981); Allen (1982)									
Natural glass stability			x						
Grandstaff (1976); Haaker and Ewing (1980); Floran et al. (1981); Smellie and Rosholt (1984)									
U-Th mineral signatures/stabilities			x		x				
Paces (1969); Benes (1980); Miekley et al. (1984); Wahlgren and Orlandini (1982)									
1. Radionuclide mobilisation and complexing (e.g. U, Th, Ra etc.)				x			x	x	
2. Morro de Ferro									

Geochemical processes

1. - Thermal/chemical stability of the buffer and seal materials
2. - Waste package corrosion
3. - Waste form dissolution and breakdown
4. - Solubility and speciation of radionuclides
5. - High temperature mineralogical fixation
6. - Radiolysis
7. - Redox equilibration
8. - Retardation during transport in the far-field
9. - Matrix diffusion

Natural analogue	1	2	3	4	5	6	7	8	9
Brimhall (1979); Brookins and co-workers (1981, 1982, 1984); Wollenberg et al. (1984); Laul and Papike (1982, 1984)									
1. Metamorphic rocks: contact metamorphism (qtz. monzonite)					x			x	
2. Evaporites: contact metamorphism (lamprophyre)					x			x	
3. Basalt: contact metamorphism (rhyodacite)					x			x	
4. Tuff: contact metamorphism (dacite)					x			x	
5. Porphyry copper deposits (Butte)					x			x	
Helgesson et al. (1969); Storey and Lintern (1981); Cramer (1983)									
Low temperature granite alteration					x			x	x
Elders et al. (1979); Giggenbach (1981); Chapman and Milodowski (1982); Vidale (1982); Elders and Cohen (1983); Tammemagi et al. (1983)									
Active geothermal systems					x				
IAEA (1975, 1978); Curtis and Gancarz (1983)									
Oklo natural fission reactor			x			x	x	x	
Batulin et al. (1965); Adler (1974); Dahl and Hagmaier (1974); Granger and Warren (1974); Rackley (1976); Rosholt et al. (1965); Osmond et al. (1983); Osmond and Cowart (1976); Andrews and Kay (1982)									
1. Roll-front sandstone uranium deposits				x			x	x	
2. Natural series radionuclide behaviour across a redox front within sedimentary strata and in associated hydrological regimes				x			x	x	

Geochemical processes

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7. - Redox equilibration
8. - Retardation during transport in the far field
9. - Matrix diffusion

Natural analogue	1	2	3	4	5	6	7	8	9
Paces (1969); Fröhlich et al. (1980); Pearson et al. (1983); Shirvington (1983); Airey et al. (1983, 1984); Andrews and Pearson (1984); Krishnaswami et al. (1982); Hubbard et al. (1984); Hussain and Krishnaswami (1982); King et al. (1982)									
1. Uranium deposits and associated groundwater systems				x			x	x	
2. Radionuclide retardation in hydrological regimes								x	
Mackenzie et al. (1983); McKinley et al. (1984)									
Geochemistry and isotopic studies of modern sediments (shorter time-scale of around 6000 years)								x	
Coughtrey and Thorne (1982a,b); Coughtrey et al. (1983)									
Measurements of bomb fall-out and nuclear released radionuclides (soils and recent marine and lacustrine sediments)				x				x	
Cramer and Gascoyne (pers. comm.); Shea (1983); Smellie and Rosholt (1984)									
1. Chemical and isotopic investigations of fracture alteration zones in the Lac du Bonnet batholith									x
2. Uranium distributions and petrofabric studies around hydrothermal vein deposits hosted by granitoids and metavolcanics									x

Geochemical processes

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Full-scale tests show the re-saturation of a bentonite buffer to proceed relatively evenly despite the localised nature of water-bearing fissures. The buffer will provide a hydraulic barrier very soon after the outer skin saturates and any construction gaps close. Total resaturation will take a number of years, after which clay pore waters will contact the waste package surface. At this point the transport of material to (oxygen, anionic corrodants, "unreacted" groundwater) and away from (corrosion products, radiolytic and corrosion generated gases, radionuclides) the packages will be controlled by diffusion through the pore space in the bentonite. Negligible flow of water will occur owing to the low hydraulic conductivity, and it is not yet certain whether gas flow (as opposed to diffusion) will be a significant transport mechanism either. Owing to the low diffusivities of all species in the highly tortuous porosity, and the complex electrostatic surface charges on the clay particles, transport through the clay is extremely slow for most ionic species. Colloidal and particulate species will probably be unable to pass through the pore structure.

The slow transport rate in both directions across the buffer is the fundamental control on the rate of release of radionuclides to the groundwater, and is a very important factor in safety assessments. Consequently, it is important to be able to predict the long-term behaviour of the saturated clay in terms of any changes in its physical properties which might be brought about by either the thermal transient of the waste, or by chemical interactions with the porewaters or the waste and its packaging. The timescale of interest during which the buffer should retain its low hydraulic conductivity is in the order 10^5-10^6 years.

Smectite-rich clays are known to transform progressively to illite if they are subject to elevated temperatures and if sufficient cation exchange can take place with potassium from porewaters. In geological sequences this transformation comes about as a result of progressive burial and heating during sedimentation (during development of a deep basin, for example) and can take millions of years. Illitic clays have higher permeabilities and lower swelling potential than smectities, and the smectite-illite conversion is consequently seen as detrimental to long-term repository performance. Since partial transformation at least is almost inevitable under long-term repository conditions, it is important to be able to assess how long this is likely to take and if there is a threshold temperature which would lead to accelerated conversion.

The temperature, pressure and chemical conditions in and around the backfill and buffer are reasonably well established, so the use of natural analogues to assess this problem is very appropriate.

Essentially two types of analogue exist. The first is the examination of thick sequences of sediments of well known ages whose temperature and pore fluid chemistry history during burial can be accurately assessed. By examining the mineralogy of the clays, an approximate rate of conversion or illitisation can be calculated. Temperature and an adequate supply of K ions are the most critical parameters. Given the availability of sufficient potassium, temperature values above about 100°C are known to induce relatively rapid illitisation, whereas at the 80°C or so defined by KBS for a maximum repository temperature, the process is very much slower. Consequently the analogue should be chosen to be representative of long periods at modest temperatures. In the NAGRA concept the buffer close to the packages is currently estimated to be subject to temperatures of 140°C or greater within some decades of disposal. However, it is unlikely that the clay would be fully saturated at this time, and the opportunity for conversion is likely to occur during later, longer periods of time at lower overall temperatures, when pore fluid is more readily available.

The second type of analogue is the case where an igneous intrusion has induced much higher temperatures in a clay, but on a much smaller scale. Since the clay may be already compacted and a thermal gradient away from a contact is present, this is a good physical analogue for a waste container. Although the contact temperatures are a good deal higher (approx. 800-900°C) than envisaged in a repository the opportunity exits to study clay properties over a thermal profile and to consider the local behaviour of pore fluids on heating.

Various studies of the first type of analogue (e.g. Eberl and Hower, 1976; Roberson and Lahann, 1981) have been made on sediments in the Gulf zone (USA) and elsewhere, generally related to petroleum exploration drilling. Observations from borehole cores have been correlated with laboratory extrapolations and theoretical models of illitisation. Illitisation is a two-stage process which requires heat in the first stage to produce a high lattice charge by replacing silicon atoms with Al, Mg (etc.), and a supply of K-rich fluid for the second stage when K saturates the exchange sites and causes collapse of the smectite to an illite structure (Anderson, 1983). The natural analogue data available showed immediately that the rate of illitisation is very much slower than predicted by kinetic models based on uniform supply of K ions (Howard, 1983). Kinetic models estimated 100% transformation in 100,000 years. However, in mixed porewater environments the observed rate is less than 0.3 % change/million years.

Granite groundwater chemistry is generally K-poor, with higher Mg contents, which tend to retard the illitisation process. For these groundwaters Anderson (op. cit) estimated that 10^5 pore volumes must pass through the clay to effect a complete change - taking 10^8 years. Thus while the data of Eberl and Hower (op. cit) give an absolute minimum time to change of 10^4 years, the natural analogue data applied to typical granitic groundwaters suggest at least 10^7 years to total transformation, even at a constant temperature approaching 100°C. This is considerably longer than the stability time required by KBS or Nagra safety studies.

A natural analogue intermediate between the first and second type described above (in that it was subject to relatively high temperatures but not as a result of an igneous intrusion) was studied by Altaner et al (1981, 1982) and is described by Anderson (op. cit):

> "Altaner et al. have identified a location in the State of Montana where a pure bentonite (smectite) bed lies between two rock strata that contain potassium-bearing minerals. These rocks were formerly buried and subject to groundwater permeation. Illitization is nearly complete at both contacts. The extent of conversion of smectite to illite was observed to diminish in a roughly exponential manner with distance inward. Independent isotope ratio measurements have established that this bed experienced environmental temperatures for a sustained period of time of 100°C to 200°C. The time involved has been reliably estimated to be approximately 3 x 10^6 years. Alteration in whole or in part has affected roughly half of the smectite in the 2.5 m thick smectite layer. Clearly the conversion, **even when the temperatures rise to levels sufficient to create the high lattice charge smectite and K^+ is readily available**, is very slow. Clearly it is limited by the rate at which potassium ion can saturate the exchange complex and lead to lattice collapse to the illite configuration. In the case of the Montana bentonite deposit potassium ions must have entered the bed by diffusion since alteration upward from the bottom of the bed almost exactly matches the alteration profile from the top of the bed downward."

A well documented example of the second type of analogue relates more to the use of medium plasticity clay as a host rock rather than a buffer. ENEA (1982) have studied the thermal effects of intrusion of a dyke (estimated maximum temperature of 800°C) into an illitic clay at Orciatico (Italy). Even at these elevated temperatures there is no evidence of any change in physical or chemical properties of the clay at distances greater than 2 m from the contact.

In this case montmorillonite was actually formed in the altered clay, possibly as a result of groundwater permeation through a porous partially baked and metamorphased zone a few centimeters from the contact.

This particular analogue cannot be applied directly to the KBS-Nagra concepts owing to the different mineralogy, but is indicative of the limited range of thermal effects (for example for in-tunnel disposal) even at very high temperatures, presumably sustained for a long period.

While analogues exist for bulk clay behaviour, there at present appear to be no data available on analogues of the sealing (contact or bonding) properties of a plastic clay. This factor is of significance in the plugging of shafts and boreholes (and also in ensuring no preferential flowpaths exist along galleries in a repository) since the major line of weakness with any seal is along its interface with the rock. Although it may be possible to find localities where flow conditions can be assessed around the clay covered margins of a granite, for example, this is not considered worthwhile since the mode of deposition of the clays is likely to be much different to a repository seal system. It is probable that seal bond behaviour, along with more general flow modelling, is something to which natural analogues are inappropriate.

The same problem exists for other seal materials which might be used locally in a repository - bulk properties can be amenable to analogue study, bonding behaviour will not. Recent work on archaeological analogues of cement based building materials (Shin, 1982; Langton and Roy, 1984) for example, has tended to concentrate on the matrix stability. A recent review of sealing techniques (OECD/NEA, 1980) concluded that natural material (pozzolans, bitumen, boulder clay, etc.) may have the most predictable long-term behaviour (above cement or resin based compounds) since they can be observed in nature. However, no attempt is known of to seek realistic or appropriate analogues for the long-term bulk behaviour of these materials under the geochemical conditions of a granite repository. Since they are only likely to be used at a distance from the waste heat source, the main issue will be to assess their stability in granite groundwaters.

5.1.1 Conclusions

- The progressive decay in bentonite hydraulic properties caused by illitisation is expected to take at least 10^7 years under the chemical and hydrogeological conditions of a crystalline rock repository, even if temperatures remain as high as 100°C for the whole period, and even if there has been a short higher temperature (ca. 150°C) early thermal transient. Even after illitisation, hydraulic and other properties might remain acceptable.
- Although the range and scale of physical changes in a heated clay appears to be very limited (e.g. to a zone of two metres from an 800°C source) there is scope for obtaining better analogue data for application to NAGRA's relatively high temperature in-tunnel disposal concept, using minor igneous intrusions into smectite clays.
- Assessment of the long-term physical bonding properties of clays (and other seal types) to the host rock does not appear to be amenable to natural analogue study.

5.2 Waste-Package Corrosion

In both the NAGRA and KBS concepts the waste-package or canister is expected to isolate the high-level radioactive waste from the environment for a long period of time. The durability of such a canister at the depths of containment envisaged, at maximum temperatures of 80°-140°C (KBS and NAGRA calculations respectively), and in contact with groundwaters, is of obvious importance. As a result, both KBS and NAGRA have conducted thorough studies on the expected life-times of the proposed canister types.

The KBS programme envisages encapsulating spent nuclear fuel in copper canisters or enclosing steel containers of vitrified high-level radioactive wastes in a copper overpack. Where an inner steel container is used for vitrified waste (KBS and NAGRA) it is generally attributed zero value as a barrier, although this is of course conservative. Unalloyed copper, prefabricated from oxygen-free forged copper, has been chosen because of its thermodynamic stability in pure water. Two alternative encapsulating methods are being considered: electron-beam welding with lead comprising the packing material around the spent fuel assembly, and hot isostatic pressure sealing with powdered copper as the packing medium. It is thought that any potential corrosion will be the result of corrodants supplied by the circulation of groundwater in contact with the canister (e.g. dissolved oxygen and sulphide), which is estimated to be one litre/m^2/year, or by radiolysis (gamma and neutron) of the water in contact with the canister surface.

Investigations (Bresle at al, 1983; Benjamin at al, 1983; Swedish Corrosion Research Institute, 1983; Tekniska Röntgencentralen AB, 1983) have been carried out to assess the reliability of the copper canisters over the long periods of time necessary for high-level radioactive waste disposal. In general, the conclusions are reassuring provided that an adequate canister wall thickness is employed; a thickness of 100 mm is thought to be adequate to sustain canister integrity for a period of 10^6 years. However, in the KBS safety analysis of the repository, it is assumed that breaching of the copper canister will eventually occur, and the reference case calculations take a first canister penetration after about 100,000 years. Penetration of the canister may be due to normal corrosion and pitting processes (a pitting factor of 5 is deemed reasonably conservative with a factor of 25 in an extremely unfavourable case), which will be irregular in extent and may also be accelerated in areas of inherent weakness caused by fabrication defects, faulty seal contacts, or mechanical weaknesses incurred during or after burial (e.g. stress corrosion cracking phenomena). Safety analysis evaluations are based on the following assumptions; (a) corrosion due to sulphide and oxygen can proceed without mutual interaction, (b) transport resistance arising from the volume increase due to the formation of low-solubility corrosion products is neglected, and (c) the copper or lead fill in the canister provides no barrier.

It has been shown (Swedish Corrosion Research Institute, 1983) that free oxygen and sulphide are the substances most likely to lead to corrosion. Although free oxygen in the groundwaters at the depths envisaged for burial (ca. 500m) should be virtually absent, small amounts of atmospheric oxygen will be trapped in the buffer and especially in the tunnel backfill materials. Even though oxygen in the backfill material is expected to migrate preferentially to the surrounding rock (rather than diffuse through the buffer material to the canister surface) where it should be readily removed by reaction with Fe (II), the possibility still exists of excess oxygen being available for corrosion. However, this source of oxygen, as well as pitting effects, are included in the KBS estimated of a canister life in excess of a million years.

Radiolytic decomposition of water nearest the canister surface by gamma and neutron radiation has also been examined, and must be taken into account even though this process is not considered to pose a major problem, even if the containers are only a few centimetres thick (Swedish Corrosion Research Institute, 1983).

Sulphide corrosion of the copper canister depends on the availability and quantity of sulphide ions supplied by the circulating groundwater, and the amount already contained within the buffer and tunnel backfill materials. From deep groundwater studies, sulphide ions are often present although usually limited by the presence of iron and the formation of insoluble iron sulphides. In the preparation of the buffer material the sulphide content is restricted to about 200 mg/kg, and is mostly in the form of iron sulphide.

Formation of sulphide by reduction of sulphate can occur through microbiological processes; without such a catalyst the reduction process is extremely slow at temperatures less than 200°C. Microbial activity will, however, be limited by the availability of energy and nutrients (e.g. McKinley at al, 1984b).

In the NAGRA concept the overpack consists of about 25 cm thickness of cast-iron. For the safety analysis of the disposal system it is not required that the container has such a protracted lifetime as proposed by KBS, in fact the reference lifetime is conservatively taken to be in the range 1000-10,000 years compared to 100,000 years for the KBS study. The main corrosion mechanism proposed is direct attack by water under anoxic conditions

e.g. $Fe + 2H_2O \rightarrow Fe(2+) + 2OH(-) + H_2$

This is taken to be a reasonably conservative mechanism since initial corrosion by dissolved oxygen in the re-invading groundwater, or by other anions in solution would tend to form a passivating layer of corrosion products which would hamper further attack. The NAGRA model uses a pitting factor of 3, and conservatively assumes that the iron container is progressively transformed into a porous oxy-hydroxide mass at a constant rate.

The canister is assumed to fail mechanically after corrosion has occurred to a depth of ca. 5cm and the time required is calculated using a rather pessimistic, empirical corrosion rate. Even after failure, however, the remnant iron and corrosion products will act as an important long-term redox buffer.

Since both the KBS and NAGRA corrosion models are highly conservative, it would be useful to obtain natural analogue data where metals have been subject to both oxic/anoxic corrosion, and attack by chloride, sulphide, etc. Care must be taken that such analogues are reasonably representative of disposal conditions in terms of availability of corrodants, and in this respect many natural and archaeological analogues are often rather poor.

5.2.1 Natural Analogues for Copper Corrosion

Although not natural analogues in the true sense of geological time, studies of the corrosion and weathering of archaeological artefacts (Johnson and Francis, 1980; Bresle et al, 1983) can provide some insight into the durability of copper over the last 8,000 years. From the standpoint of early weaponry and tool fabrication, native copper has been one of the most important natural metals. Such artefacts date back to 6,000 BC and smelting/casting had become established by 3,000 BC. Examples are numerous of copper articles having survived well in moist surface environments in direct exposure to the elements, although it was thought necessary by some groups to protect copper by coatings of mercury, solder and lead. In general, however, copper has an impressive record of durability on land and in seawater. A study of 34 archaeological artefacts composed of copper, bronze and brass (Johnson and Francis, 1980) revealed corrosion rates of 0.025-1.27 micron/year. On assuming a canister thickness of 10cm (KBS-3), this would correspond to penetration times under oxidising conditions of 80,000 - 4,000,000 years.

Pitting values of archaeological artefacts, ranging in age from 300 to 3,000 years, have been measured by Bresle et al (1983). There are, naturally enough, many limitations in interpretation due to the large variability of metal composition, exposure time, soil conditions, etc. Measured pitting values recorded maximum values of only around three, well within the conservative value of 25 assumed by KBS (i.e. the largest value observed by Denison and Romanoff, 1950, in their study of buried copper samples in various soil types over an exposure period of four years). Furthermore, a piece of native copper, which had lain in soil for at least 8,000 years, exhibited a pitting factor of only 2-6.

In a geological context, native copper occurrences are fairly widespread with the largest known deposits being found in Northern Michigan (Butler and Burbank, 1929; White, 1968). Three types can be recognised: (a) conglomeratic lode types, (b) amygdaloidal lode types of volcanic origin, (c) fissure deposits. The native metal has a very low impurity content (99.998 wt. % Cu) and has been exploited from earliest times (4,000 years ago). Copper boulders have been located in glacial outwash areas, having been left there during the last melting stage of the glaciers (estimated to be at least 8,000 years ago). During this time the boulders would have been subjected to extremes of temperature, moisture and intermittent glacial meltwater (ph = 5-6), yet they presently show only thin oxide layers.

Johnson and Francis (1980) compared abraded faces (i.e. a minimum of 8,000 years) with unabraded faces (i.e. pre-glaciation surface), and found that the former was characterised by a very thin oxide layer (0.07-0.60mm) and the latter by appreciably thicker layers (up to 2mm). Extrapolation of these data indicate that it would take considerably longer than one million years to oxidise a 10cm thickness of copper, even under such extreme conditions.

The occurence of native copper associated with large quantities of gypsum, at Coro Coro in Bolivia (Lindgren, 1933), is interesting in illustrating the prolonged existence of the metal in the presence of sulphate and may thus be worth more detailed study.

A study is presently being carried out in Sweden of the mineralogical and textural associations and stability of native copper in specimens collected from different locations and rock-types, and representing mainly oxidising environments.

5.2.2 Natural Analogues for Iron Corrosion

Native iron metal is a geological rarity and is usually alloyed with a small percentage of nickel. Masses of up to 20 tonnes are reported associated with basalts from Disko Island in Greenland (Johnson and Francis, 1980). No work is known of which has assessed the corrosion behaviour of these deposits, and this is considered to be worth following up.

Iron meteorites (nickel-iron alloys) have been assessed by Johnson and Francis (op. cit) as possible analogues of iron waste containers, but owing to the problems of assessing the varied environmental conditions to which the materials have been subjected, the results are qualitative and inconclusive. A wide variety of corrosion rates and mechanisms were identified, with some samples surviving up to 20,000 years. Further work in this area is unlikely to be productive.

The corrosion rates of iron objects from the archaeological record shows a remarkable uniformity, as estimated by Johnson and Francis. Discounting two examples of rapid corrosion (iron cannonballs in seawater) as inappropriate, all of the remaining 42 examples assessed show corrosion rates of 0.1 to 10 micron/year (a few samples having rates as low as 0.01 micron/year). The specimens came from a very wide variety of environments, dry, wet, oxic, anoxic, etc. Some Roman iron objects assumed to have undergone anoxic corrosion in the wet detritus of an old well, show a corrosion rate of one micron/year. This corresponds to a mechanical failure time of about 5×10^4 years, or a corrosion penetration time of 2.5×10^5 years for the NAGRA container. Even at the upper end of the rate estimates some iron in the container might be expected to survive for at least 10,000 years, although mechanical failure or pitting could cause failure after only about 2000 years.

Dressalaers and Casteels (1983) report corrosion rates under presumably oxic conditions for cast iron tunnel supports from a 90 year old coal-mine which have been in contact with marly soils. These are of the order of 10 micron/year and correlate reasonably with the archaeological data. The rates are presumed to be higher than would occur in a granite repository owing to the open system oxic conditions.

As noted earlier, archaeological analogues must be approached cautiously. Nonetheless the more applicable analogues point to considerable longevity of containers when compared to the 1,000-10,000 year lifetime assumed by NAGRA. These types of analogue, selected carefully, would merit further study, particularly to assess the evidence for the corrosion pitting factor for which no data are currently available.

5.2.3 Conclusions

- Natural analogues for iron corrosion are rare. Meteorites appear to provide poor and ambiguous evidence for the corrosion behaviour of Ni-Fe alloys and are probably not worth considering further. Further native iron deposits could provide useful data but have not been studied (to our knowledge) with this in mind.
- Archaeological analogues of iron corrosion provide surprisingly consistent rate data from a wide range of environments. The most appropriate data indicate a total corrosion time for the NAGRA container of at least 250,000 years, with possible mechanical failure after 50,000 years.
- Natural analogues for copper corrosion, in the shape of native copper masses, indicate considerable longevity (more than 10^6 years) for a 10cm thick container, even under extremely unfavourable open system, near surface oxidising conditions.
- Archaeological data on copper corrosion, again for a wide variety of environmental conditions (but all oxidising) give shorter life-times than natural analogues, predicting values between 80,000 to 400,000 years for a 10cm thick container. Conversely, the pitting factor (25) selected by KBS seems highly conservative when compared to a value of 3 determined from archaeological materials.

5.3 Waste-form breakdown

The waste matrix may be either a borosilicate glass or uranium oxide spent fuel in both the Nagra and KBS concepts. Other HLW waste forms are also being considered in a few other countries (particularly the USA) as alternatives to these matrices. These come under two broad categories: glass-ceramics and super-calcines. They are characterised by being either partially or fully crystalline and, depending on type, may comprise a wide or carefully restricted variety of minerals which have counterparts in nature. One such waste-form is the three-phase titanate SYNROC-B comprising perovskite, hollandite and zirconolite. Other crystalline waste forms contain silicate minerals or analogues of oxides such as rutile and spinel. The man-made minerals differ from many of their direct natural analogues in containing a wider variety of elements either structurally bound or in solid-solution, and are of course much more radioactive and thus prone to radiation damage. Studies of both active and inactive natural analogue minerals have proved highly rewarding in terms of assessing the long-term behaviour of their man-made counterparts. However, since such waste forms are not currently under consideration in Sweden or Switzerland, the result of these studies are not considered further here. The interested reader is referred to Haaker and Ewing (1980, 1981) and Ringwood et al, (1980), as a starting point. Returning to the spent fuel/ glass waste forms considered here, the release of radionuclides to leaching groundwaters is, to a large extent, dependent on the rate and mechanism of breakdown of the matrix itself. The processes of interest in assessing the behaviour of the waste form can be summarised as:

a) Mechanism of attack by water

b) Formation and composition of surface layers

c) Rate of release of specific elements and possible uptake or precipitation in the surface layer

d) Long-term stability (only in terms of devitrification of glasses).

Evidence for the behaviour of both active and simulated HLW glass when subjected to attack by groundwaters comes from what is by now a considerable quantity of laboratory experimental data. Glass leaching has been simulated under a wide spectrum of pressure, temperature and flow conditions, in open and closed systems, and in the presence or absence of other engineered component or host rock materials.

It is now appreciated that only either closed system or very slow flow conditions will produce appropriate data on the release of radionuclides from the matrix. At low temperatures the glass network breaks down by hydrolysis and an amorphous or poorly crystalline surface layer builds up. Radionuclides are released during the process of matrix dissolution and their concentration in solution is determined by the chemical equilibria between the leaching groundwaters, the glass and the newly formed alteration products. At low temperatures the kinetics of this process is very slow, and the rate of release of individual radionuclides to solution is very variable (by several orders of magnitude, see for example Savage and Chapman, 1982). As the surface layer builds up, the rate of reaction is controlled by water and solute diffusion through it, as well as through the clay buffer and the canister corrosion products. A fully realistic analysis of this complex physico-chemical environment has never been carried out, assessments always tending to be simple and highly conservative.

Experimental data on spent fuel dissolution are much sparser, although the same basic processes occur. The crystalline uranium dioxide matrix is progressively dissolved by water, although a passivating layer of corrosion products can be formed which hampers further dissolution. Spent fuel breakdown is an extremely slow process controlled by the solubility of uranium in the groundwater, presumably in a surface oxidising micro-environment (e.g. Werme, 1983; see also section 5.6). Certain radionuclides will form either as or in discrete intergranular or intragranular phases and may be released at a rate independent of the breakdown of the fuel matrix. Others may diffuse in the solid state to grain boundaries where they are more easily mobilised, on the time scales likely for spent fuel dissolution.

Analogues of both glass and oxide waste forms exist in nature as volcanic glasses and as uraninite (UO_2) ores, and both have been extensively studied. The two waste matrices are considered separately.

5.3.1 Analogues of vitrified waste

The fundamental problem with applying data on volcanic glasses to borosilicate glasses is their considerable difference in composition.

Massive volcanic glasses are formed by very rapid cooling of flows or injected magma such that few crystals are able to nucleate. They can range in composition from rhyolitic obsidians with more than 80 wt % SiO_2, to basaltic glasses with around 50 wt %, very similar to waste glass silica contents. However, the basaltic glasses contain no boron or lithium, being alumina and iron-rich. The dissimilarity in breakdown behaviour between borosilicate and high-silica glasses has been known for some time in the nuclear industry, and makes direct comparison difficult. The high- silica glasses are considerably more stable to hydrothermal attack than borosilicate glasses, both as reference waste forms and in the natural environment (e.g. Dickin, 1981).

The majority of natural glasses are less than 2 million years old, and no terrestrial glasses are known older than 40 million years according Ewing, 1979 and Malow and Ewing, 1981. However, a 1600 My old (Pre-Cambrian) glass has recently been recorded by Lindqvist and Laitakari (1980). It is generally assumed that older glasses have completely devitrified to a crystalline mass, or have been attacked by water and recrystallised. Malow and Ewing (1981) suggest that 2 million years is a useful maximum age to which radwaste glasses might be expected to survive, but admit that the natural analogues have been subject to near-surface weathering processes inapplicable to deep disposal. Devitrification is known to be extremely slow in the absence of water (e.g. before canister breaching), as evidenced by fresh volcanic glasses from the moon. It is considered here that a maximum age of some tens of millions of years may be more appropriate, but that this does not reflect a time at which the glass would lose its containment integrity, only a time at which it may be completely recrystallised. However, since all scenarios of near-field behaviour predict access of water to the waste within at most a few million years, and since the process of groundwater attack will then dominate, this age is of little use for modelling.

Allen (1982) examined low silica basaltic glasses and suggested that devitrification at low temperatures (near $0^{o}C$) would take approximately 10 million years. The geological evidence thus supports the idea that devitrification will not be a problem on the timescales of interest for performance modelling.

The process of hydration of natural glasses progresses at a rate dependent on the availability of water. Hydrated natural glasses (e.g. perlite) are known to release elements such as uranium at an increased rate compared to fresh glasses, when attacked by warm groundwaters (Zielinski, 1979). Stresses produced during cooling and hydration cause massive glass to fracture, hence increasing the surface area to volume ratio available for attack by water.

Zielinski (1980) calculates the rate of hydration of high silica glasses as about 30 microns penetration per million years at 20°C. At 120°C the process is four orders of magnitude faster. Essentially natural glasses obey the same parabolic rate laws of breakdown as do radwaste glasses (Savage and Chapman, 1982).

The thickness of hydration crusts on artefacts made of high silica rhyolitic glasses has been used quite successfully to date them for archaeological purposes. Experimental data on the development of a hydration rind by reaction with largely atmospheric moisture have been extrapolated to give rate data. Kaplan (1980) describes the corroding effects of atmospheric moisture on ancient man-made glasses, but owing to the gross compositional differences the data cannot be applied to radwaste glasses. Natural obsidian glasses chemisorb water onto their surfaces which then diffuses into the glass and breaks down the structure. However, laboratory data generally tend to produce lower diffusion and reaction rates than are found in nature (Ericson, 1981). Basaltic glasses alter rapidly when large amounts of water are available. The process of developing an iron-rich clay rind (palagonite) appears to protect the glasses from further attack for periods of some millions of years (Allen, 1982). Uranium and some REE's are preferentially incorporated in this crust as the glass breaks down (La and Pr in particular, but not Ce). The crust may also contain strongly sorbing zeolites such as chabazite and analcite.

Generally these observations support mechanistic studies of waste glass breakdown. As such they represent useful signposts, but owing to the compositional differences are of limited quantitative value. Perhaps one of the more important conclusions is that the armouring effect of a leached layer can persist for some millions of years if the rate of access of water is limited. However, none of the studies reported here has been able to link-in the time factor for other than archaeological materials. It has not been possible, for example, to assess the time and rate of access of groundwater to a body of un-devitrified natural glass in such a way as to calculate the actual alteration rate.

The general conclusion of this analysis is thus that natural glasses cannot be used as precise analogues and can only give the most general qualitative support to glass breakdown models. Two more positive findings are, however, worth noting:

- Devitrification is not a problem on the timescale of interest provided temperatures remain modest. However, the effects of radiolysis and recoil, not normally seen in natural glasses, need to be considered in this respect.

- Under limited flow conditions as might be anticipated in a granite repository the theoretical lifetime of a glass block prior to recrystallisation consequent on hydration could be in the order of 10^7 to 10^8 years provided the surface area/volume ratio is low.

5.3.2 Analogues of spent fuel

Unreprocessed spent fuel comprises a matrix of crystalline uranium oxide (UO_2) containing the fission product and transuranium elements either within the crystalline structure or loosely held in intercrystalline spaces. A proportion of some fission product elements (e.g. I and Cs) may be free to migrate within the matrix porosity of the fuel. The UO_2 crystals have the structure of fluorite and some fission product oxides (e.g. CeO_2) enter into solid-solution with this structure. Freeborn et al. (1982) surveyed more than two dozen papers and concluded that very little else was actually known about the crystalline structure of spent fuel.

Uraninite (UO_2), a natural uranium ore mineral also with a fluorite structure, is a close analogue of spent fuel except that it has normally not been subject to the intensive neutron flux and fissioning of a nuclear reactor. Consequently the large inventory of fission products is not present, and structural weakening of the matrix by bombardment and recoil has not occurred. However, the stability of uraninite under radiation damage remains high (Haaker and Ewing, 1980). In fact, uraninite displays no metamict state, and its rate of oxidation or dissolution are more dependent on its chemistry than on its structure (Grandstaff, 1976). This detailed study of the dissolution behaviour of natural uraninites under different conditions of pH, oxygen activity and carbonate activity provides an excellent natural analogue comparison for the rate and mechanisms of spent fuel breakdown.

Mineralogical studies and uranium-series disequilibrium measurements on Proterozoic uranium vein deposits in N. Sweden are reported by Smellie and Rosholt (1984). Mineralised samples for depths ranging from 55-130m showed that rock-water interaction processes, and resultant radioactive disequilibria, characterised most of the samples. The isotopic disequilibria are explained by ^{234}U recoil-induced loss or gain; little ^{238}U has been removed from any of the samples suggesting that no oxidative bulk leaching has occurred during the last 0.5 Ma. That reducing conditions normally prevail at these depths is demonstrated by the mineralogy which shows that uraninite has remained texturally stable for most, if not all, of its 1750 Ma existence. By analogy, it has been suggested that these results would tend to support, at least to the depths investigated, that other actinides with similar chemical properties to uranium and which are present in high-level radioactive waste, would also have been stable in this environment for similar periods of time.

Exceptions to these normal occurrences of the mineral are the core zones of natural fission reactors such as Oklo, where the uraninite should most closely resemble spent fuel. The following description of the natural reactor in the uranium ores at Oklo in the Gabon, is modified and translated after Brookins (1984):

> "The Oklo uranium ores consist of syngenetic to early epigenetic sandstone type deposits formed about two billion years ago. Some of the early-formed ore was remobilised during folding and faulting relatively soon after sedimentation-mineralisation. This remobilised ore was transported into zones of locally reducing conditions, where the uranium was again precipitated, in places reaching contents of 50-70%. The remobilised uranium was effectively segregated from most of the elements associated with it in the low-grade ore. These other elements, had they been remobilised with the uranium, would have prevented any nuclear reactions from taking place as they would have served as neutron poisons. The ores that sustained the fission reactions consist of pitchblende with gangue chlorite and illite.
>
> Two billion years ago the ^{235}U content of normal uranium was about 3.2%, in the range to which modern uranium (with 0.7% ^{235}U) is enriched for use in man-made nuclear reactors. Criticality was achieved in the Oklo ores owing to the presence of a favourable water: uranium ratio and the lack of neutron poisons. The water content of the rocks in which the remobilised uranium was precipitated was probably in the order of 12 to 15%; a higher or lower water content would not be efficient as a neutron moderator. Criticality was achieved during or soon after the precipitation of the remobilised uranium, about two billion years ago and continued for at least 500,000 years, during which time some 15,000 MWe-years of energy were generated. About 800 tonnes of uranium took part in the reactions and some 10 tonnes of ^{235}U underwent fission. Smaller amounts of ^{239}Pu and ^{238}U also underwent fission. The fission reactions presumably ceased as water was driven off by the locally high (400°C) temperatures, and as the fission products built up to act as neutron poisons. More than 10 tonnes of fission products were produced, which are identical to the fission products from man-made nuclear reactors. The depth to which the Oklo deposits were buried is estimated to be approximately 3,500m."

The core zone of the Oklo reactor (some 1,800 million years old and composed of uraninite surrounded by pitchblende and altered gangue minerals) appears to have retained its structure without alteration of the uraninite grains.

The ^{235}U-depleted grains resulting from fission within the reactor zone are intact except for the outer micron or less (Duffy, 1978) indicating exceptional stability to attack or recrystallisation in the geological environment. The escape of fission products from the uraninite was controlled by their diffusion out of the fluorite structure of the grains, rather than by dissolution and attack of the mineral itself (Cowan, 1978). Laboratory and theoretical data show the dissolution of UO_2 to be strongly dependent on the temperature and carbonate content of the water (Allard, 1983). Alpha radiolysis may mean that truly reducing conditions cannot exist around spent fuel for at least the first 10^5 years after disposal, (Johnson et al., 1983), which may account for apparent insensitivity to redox conditions in experimental studies (Johnson, 1982) compared to a strong theoretical dependence for natural UO_2. The natural analogue evidence for radiolysis at the surface of uraninite grains in the Oklo core zone, although somewhat ambiguous, seems to support this idea (see section 5.6).

The hydrochemical, thermal and groundwater regimes at the time of the reactor event, and its temporal and spatial propagation are, however, difficult to assess. There are thus some practical problems in applying the Oklo data, owing to ill-defined boundary conditions. Among these is the fact that the uraninite matrix probably formed as a result of recrystallisation during the reactor period, and the siting of both fission products and transuranics (and their consequent mobilisation behaviour) in the matrix is likely to be somewhat different to spent fuel. However, several points make the Oklo phenomenon usefully conservative as an analogue for spent fuel disposal

- The timescale (approx. 2 x 10^9 years) is very much longer (by at least three orders of magnitude) than that over which near-field containment of the waste is considered important

- Temperatures and consequent hydrothermal activity were considerably higher (greater than 400°C) than envisaged for disposal

- Accessibility of groundwaters to the uncontained UO_2 has been maintained from the reactor period onwards.

On the negative side, the burn-up rate at Oklo is undoubtedly modest when compared with spent fuel, and the consequent intracrystalline mobility and concentration of fission products, together with the possible development of gas bubbles and separate fission product phases at grain boundareis, all of which would tend to weaken the UO_2 matrix, are all much less developed than in fuel elements. The two most impressive features of the Oklo core zone are:

- The retention of structural, mineralogical and isotopic integrity of the final matrix UO_2 over a timescale of 10^9 years despite accessibility to groundwater
- The dominance of inter and intracrystalline diffusion as the release mechanism for fission product elements from the matrix once the reaction had ceased.

The scope of Oklo as a natural analogue is more wide ranging than simply assessing the core zone from the viewpoint of waste dissolution. It also provides useful evidence on radiolysis (see section 5.6) and the migration behaviour of the fission products (assessed in more detail in section 5.8). While the chemical conditions are difficult to assess precisely, the probably mildly reducing to oxidising conditions and apparent lack of carbonate complexation indicate a relatively benign environment for uraninite preservation. In a granite repository redox conditions may be more reducing if a buffer (e.g. massive iron container) exists to control radiolytic oxidation, although carbonate availability may be higher. However, it is felt that disposal conditions are unlikely to differ considerably from those in which the Oklo core zones have existed for billions of years. This particular analogue, considered more applicable than those related to normal uraninite ores, indicates that the predicted extremely protracted lifetimes for UO_2 fuel elements are in fact adequately justified.

5.4 Solubility and Speciation of Radionuclides

The speciation of any radionuclides in aqueous solution is determined by a large number of reactions including redox redistribution between possible oxidation states, hydrolysis, complexation with available organic or inorganic ligands, ion pairing and polymerisation. This speciation will define the maximum aqueous phase concentration, above which precipitation of thermodynamically or kinetically stable solids will occur, which is obviously of great importance in waste dissolution (5.3) or high temperature mineralisation (5.5) processes. The actual solute chemistry, and in particular the distribution or radionuclides between possible anionic, cationic and neutral species, will greatly influence the magnitude of retardation experienced during fissure flow (5.8) or matrix diffusion (5.9). In this section only natural analogues for speciation and solubility in the far-field will be considered, without consideration of redox equilibrium which will be discussed separately in 5.7. Many potential analogues exist in the geochemical literature where the chemistry of naturally-occurring or man-made radionuclides have been investigated in relevant conditions but the extent of interpretation of this information has, to date, been very limited.

5.4.1 Analogues of Speciation

In the KBS/NAGRA safety analyses, solubility and speciation are evaluated by equilibrium thermodynamic models. These are checked by comparison of predicted solution phase concentration of particular elements (e.g. U, Th) with those observed in natural groundwaters assuming saturation with respect to the least soluble solid phase (e.g. Allard, 1983; Schweingruber, 1983). In this case the natural supply of these elements by the rock is considered to be analogous to supply from the waste form. Although extensive compilations of water analyses from relevant granitic formations exist (e.g. Snellmann, 1982; Allard et al, 1983a; NAGRA, 1984), these analyses are insufficiently complete to allow rigorous examination of aqueous speciation, often require extensive manipulation to correct for sampling perturbations (e.g. Schweingruber, 1984) and generally lack details of the history of the water. Although available data are probably insufficient to allow rigorous validation of the thermodynamic speciation models, they certainly can provide ballpark figures with which such models can be compared (e.g. Langmuir, 1978; Langmuir and Herman, 1980; Schweingruber, 1983).

If a wider range of aqueous environments is considered, many more data are available. Information on the speciation of relevant elements (excluding the actinides) in soil and surface sediment environments has been summarised recently (Coughtrey and Thorne, 1982a; b; Coughtrey et al, 1983). Information on the actinides tends to be somewhat more widely scattered but may be found in the proceedings of some of the many conferences on this topic (e.g. Friedman, 1976; White and Dunaway, 1977; Hanson, 1980).

On only a very few occasions have the available data been analysed specifically as analogues of speciation. Natural Th released from the extensive ore deposits at the Morro do Ferro in Brazil has been considered as an analogue for Th, Pu (IV) and, more speculatively, trivalent actinides released from radioactive wastes (Eisenbud et al, 1982b; Miekley et al, 1982). This work has involved analysis of Th speciation in near-surface groundwater, streams and rivers and, although some indication of the proportion of Th in ionic, nonionic and "organic-acid" complexed forms can be derived from this study, the high concentration of organic carbon in such water limits its direct applicability to more relevant environments.

An alternative, well-defined source of relevant elements arises from the leaching of mill tailings from uranium ore processing. In an extensive review Benes (1980) has shown that very useful information on the natural speciation of Ra can be derived by analysis of groundwater in the vicinity of such tailings but again the high concentration of organic carbon and the possible perturbing influences of microbial activity limit direct extrapolation to deep environments.

For both examples above it should be emphasised that, while direct extrapolation to relevant environments is not justified, the data produced are again useful for qualitative evaluation of the applicabililty of equilibrium thermodynamic models or semi-quantitative comparison of alternative data bases. A further example which illustrates this approach well is the study of Wahlgren and Orlandini (1982) in which comprehensive speciation analysis of dissolved U, Th and Pu in North American lakes was compared to model predictions.

5.4.2 Conclusions

- Comprehensive groundwater analyses from target formations allow the rock itself to be used as an analogue source of several relevant elements which is extremely useful for checking thermodynamic models.
- Direct extrapolation of speciation data from near surface (soil) conditions to those expected in deep groundwater is probably meaningless for most relevant nuclides. Such information is, however, useful for evaluation of speciation models, particularly in the case of elements for which thermodynamic data are uncertain or lacking.

5.5. Mineralogical fixation at elevated temperatures

This process, whereby radionuclides released from the degrading waste form are incorporated into the structure of new minerals formed under mildly hydrothermal conditions, is only of significance if container failure occurs within the thermally active period shortly after disposal. This could be termed "hot release", and the mechanism can provide an important means of radionuclide fixation which will not be available for the majority of containers which are breached well after the thermal transient has passed.

The mechanism is only really effective if the temperature at the time of container failure is in excess of about 150-200°C (Savage and Chapman, 1982). Reaction products tend to be well crystallised and form quickly as the warm groundwaters interact with the near-field components. At the lower temperatures proposed in the Nagra-KBS concepts the hydrothermal reactions will be sluggish and the reaction products will be amorphous, dominated by clays (probably smectites buffered by the large volume of bentonite present). Whether containers fail within the thermal period or not, the rock around the disposal zones will in any case have undergone a phase of hydrothermal alteration which will involve mild leaching of alkali earth elements and silica, together with silica mass transport and deposition in fissures. These effects may well enhance the containment properties of the near-field by reducing conductivity and increasing sorption potential.

Natural analogues of hydrothermal alteration of granitic rocks caused by a warm source of "exotic" elements are very common, being provided by vein mineralisation such as pegmatites and porphyries. In addition, igneous bodies intruded into crystalline metamorphic rocks can provide similar analogues. In both cases a hot, water-rich fluid, with concentrations of elements enriched with respect to the host rock (Cu, U, REE's, etc.) is injected into the fractured crystalline host, causing localised hydrothermal reactions and thermal groundwater movement. The direct analogy is with a hot, failed waste container in direct contact with the host rock (i.e. with no buffer present).

Geological systems which have been studied with this analogy in mind include the Eldorado quartz-monzonite intruded into metamorphic rocks (Brookins, et al., 1982) and the Butte porphyry copper (Brimhall, 1979). Brookins and co-workers have applied the same approach to other host rocks; lamprophyre intruded into evaporites (Brookins, 1981b), rhyodacite into basalt (Brookins and Murphy, 1984), and dacite into tuff (Wollenberg et al., 1984). Oxygen isotope studies can be used to assess the extent of fluid circulation around the contact zones and, combined with data on mineral stabilities, the maximum temperatures attained. Depths of burial are usually consistent with suggested repository depths, although the "hot time" available for reaction is generally much longer (greater than 10^4 years) than is the case for HLW.

The Eldorado stock data show that virtually no hydrothermal circulation of fluids took place at a distance greater than 3 m from the contact, despite temperatures of 350-450°C. The movement of REE's, U, Th, Co, and Pb was restricted to this small aureole zone. Although Brookins et al. (op. cit) present no data on the fixation of these elements, it is clear that hydrothermally produced phases are responsible for the uptake of elements diffusing out of the monzonite intrusion.

Whilst analogues of this type are ubiquitous and easily studied, their use is unfortunately limited owing to the generally high temperatures involved. The majority involve processes which were operative at temperatures greater than 250°C, frequently being between 300 and 400°C. Not surprisingly reaction kinetics and the efficiency of element fixation are orders of magnitude greater at these temperatures than at 50-100°C. In addition, mineral phases found as stable reaction products at 250°C will not necessarily be present at 100°C. In fact, the stability field for granitic rock alteration products at around 50°C is dominated by kaolinite (Helgeson et al., 1969). Thus the majority of the analogues already available are inappropriate to the Nagra-KBS concepts, although indicating interesting possibilities should higher disposal temperatures be envisaged.

Moving down in temperature to the range 100-200°C it is possible to use late-stage hydrothermal vein systems in granites (generally around 150°C or more). The French study of this analogue (Jebrak, 1984) is in its early stages and no results are yet available. However, the work of Shea (1984) on a uranium vein in monzonite has produced useful data on hydrothermal interactions during a very similar mineralisation episode. A dilute, reducing, hydrothermal fluid rich in uranium (complexed as fluoride) passed through fractures in the granite at a temperature of about 150-250°C. Extensive reaction with the granite produced a new and very complex mineralogy in which the uranium precipitated out as uraninite (UO_2), forming a vein system in the unaltered host rock. This process (common in uranium mineralisation) is an ideal analogue of how fixation could occur, but once again is inappropriate (in the NAGRA-KBS context) for the following reasons:

- The temperatures involved are still too high (at 150-250°C). The reactions involved would not occur at 50-100°C in a repository

- The volumes of fluid involved are considerably greater than would be expected to pass through the near-field of a repository in its thermal period

- Although highly reducing, the corrosive hydrothermal fluid, rich in sulphur and fluorine and of initially low pH, in no way represents a reasonable "warm groundwater" in a repository environment.

Thus it appears that even the relatively low temperature vein systems in granite may be poor analogues of mineral fixation (although useful in assessing diffusion - see section 5.9). Only where a demonstrable temperature gradient has been combined with permeation of fluids away from the source to allow lower temperature interaction to occur, would this analogue type be applicable. In this respect the present work of Laul and Papike (1984) on chemical gradients around pegmatite veins may give useable data, and is discussed further in section 5.9.

We are thus forced again to move to lower temperatures, in the range 50-150°C. At the lower end of the spectrum processes approximate to natural surface weathering, although under reducing conditions and with a lower availability of CO_2. Under these conditions calcite and iron oxides are likely to be the initial fracture surface alteration products until CO_2 and oxygen are exhausted, followed by development of clays (Apps, et al., 1983). Given the dominance of kaolinite at low temperatures mentioned earlier, Apps et al. concluded that the immediate zone around a waste container might display pervasive development of this clay along all fissure surfaces, surrounded by a zone of incipient smectite alteration. While both of these clays possess favourable properties as regards sorption or rock permeabilities, they are unlikely to be responsible for strong fixation of leached radionuclides as envisaged for higher temperature reaction products of the rock and the waste form. Analogues for low temperature alteration of granites are common (e.g. Storey and Lintern, 1981) although one must be cautious that the fluids involved are representative of reducing groundwaters, and again that temperatures were not in excess of about 100°C. Similarly the volumes of fluid involved must be considered with care, since altered zones in granites can generally be assumed to have been major transmitters of fluid compared to the near- field rocks of a repository.

All of the analogues discussed above are "fossil" systems, in that the processes leading to element migration and fixation are extinct. However, it is also possible to use active geothermal systems as analogues (Vidale, 1982; Tammemagi and Parrish, 1983; Elders and Cohen, 1983; Chapman and Milodowski, 1982) and by monitoring of temperature fields and rock-water chemistries from borehole data, assess the extent of hydrothermal activity. This has the distinct advantage that indirect estimation of the important thermal parameters, as used in fossil systems, is not necessary.

Once again the temperatures involved tend to be rather high and the rock types are often mixed volcanics and sediments rather than granites. However, one important lesson has already been learned using such systems. Elders et al. (1979) demonstrated that mineralogical equilibria in the Cerro Prieto (Mexico) hydrothermal system are dependent on the temperature attained and the permeability of the rock. Mineralogical and thermal data from boreholes penetrating the geothermal zone in both sandstone and shales were used to construct contours of mineral stabilities related to temperature isotherms. It was found that low temperature assemblages persisted to higher temperatures in the shales owing to their lower permeability, and hence lower fluid flux and slower attainment of equilibrium. This situation is similar to that which would pertain in fractured crystalline rocks. The thermally active life of a repository is much shorter than that of natural geothermal systems, and combined with lower bulk permeabilities and temperatures, this suggests that reactions are unlikely to reach equilibrium and they will be extremely sluggish. The problem of using thermodynamic data for low temperature systems, was discussed by Giggenbach (1981). Whilst it may be possible to predict zonal assemblages for higher temperatures and to determine pressure and temperature conditions in fossil systems, the many metastability steps, when combined with the limited thermal life of a waste repository, make practical chemical predictions difficult.

5.5.1 Conclusions

The essential conclusions of this discussion are thus:

a) Elevated temperature fixation of radionuclides in waste-form / host rock hydrothermal reaction products is not a significant retention mechanism if temperatures remain below about 150-200°C.

b) As far as chemical retardation processes are concerned, analogues based on igneous intrusion or elevated temperature (200-400°C) mineralisation contact zones are inappropriate for the Nagra-KBS concepts (see also section 5.8).

c) Low temperature (less than 100°C) alteration in the host rock in a repository may be difficult to predict using theoretical thermodynamic data owing to the sluggish reaction kinetics caused by low temperatures and fluid fluxes.

d) The type of mineral alteration in the near-field is likely to be dominated by clays (kaolinite, although the buffering effect of the bentonite may lead to smectite formation) whose useful rôle will be sorption / permeability control at a later stage rather than direct structural incorporation of radionuclides.

This is because container failure is most likely to occur after the thermal period.

e) Late-stage, low temperature mineralised veins in granite may provide the most useful natural analogues, although they are much more applicable to diffusion processes and to assessment based on later low temperature alteration by groundwaters.

5.6 Radiolysis

An important factor in evaluating the chemistry of the "near-field" is the perturbation caused by radiation from the nuclear waste. Radiation damage to most surrounding solid materials (e.g. container) can be considered negligible at the relatively low dose rates involved, although damage to the waste matrix itself could be important and has been considered in section 5.3. The main radiation effect is thus taken to be radiolysis of water which can be represented as:

$$H_2O \rightarrow H_2O^* \rightarrow H_2,\ H_2O,\ H_2O_2,\ OH,\ O_2,\ H^+,\ e^-,\ \text{etc.}$$

The main primary molecular - or free radical - products of decomposition of the "excited" water molecule are indicated (Allen, 1961), but their proportions and the results of secondary reactions are critically dependent on a number of parameters (Christensen and Bjorgbakke, 1982) such as:

a) Water chemistry
b) Radiation type and energy
c) Dose rate
d) Availability of surfaces.

It should be noted that many of the basic radiolytic data available in the literature are derived from high dose rate irradation of pure water with a single type of radiation and thus extrapolations in terms of all the parameters listed above are required to model "near-field" radiolysis. In terms of water chemistry, radiolytic products will vary with Eh (redox potential) and pH in a fairly well understood manner but will also be very dependent on low concentrations of species which can combine with radicals or catalyse radical reactions (e.g. Fe^{II}/Fe^{III}, $UO_2 2+$) for which very few data exist. The radiation dose to the water itself is very complex, varying in space and time. The groundwater is exposed to a low LET (linear energy transfer), high intensity gamma/neutron flux prior to canister failure, and later to a high LET, low intensity alpha/beta flux at the waste surface when containment is lost. The total alpha/beta dose rate is very dependent on the available waste surface area which is poorly defined for vitrified waste, while the availability of surfaces also influences radical combination reactions and hence the distribution of radiolysis products.

The net result of radiolysis has been modelled by Neretnieks (1982) who considered that all H_2 produced was effectively inert and lost from the system by diffusion leaving an "oxidising near-field". In this model the resultant "oxidants" (such as H_2O_2) diffuse through the bentonite buffer and into the initially reducing fissure flow system. As this progresses the redox buffering capacity of the rock (modelled by Fe^{II}/Fe^{III} reactions) is gradually overcome. Enhanced solubility and decreased retardation of several important nuclides (U, Np, Tc) by several orders of magnitude would be expected in this oxidising region while precipitation or colloid formation could occur at the "redox front". Movement of a redox front and Eh buffering in natural environments are considered in more detail in 5.7.

5.6.1 Analogues of radiolysis

Because of the high levels of radiation required over long periods of geological time, the choice of natural systems for study is accordingly very limited. The Oklo natural reactor was therefore the most suitable choice because, in addition to satisfying the above requirements, its geological setting and mode of origin are reasonably well-defined having been subjected to intense study over the last 10 years. Radiolytic effects in the Oklo reactor have been investigated by Curtis and Gancarz (1983). In addition to determining the effects of radiolysis products on the rocks, they calculated the radiation doses and examined the production of radiolysis products in the fluid phase. They also attempted to answer two of the most important questions regarding radiolytic effects:

1. is there any evidence of an outward moving oxidation "front" from the reactor zone that could be attributable to the processes outlined above?

2. is there any evidence of element transport out from the reactor zone as a result of enhanced solubility and mobilisation due to oxidation effects?

In and around the Oklo natural reactor the rocks have been exposed to higher levels of radiation than any other rocks known in the earth. From the available data, Curtis and Gancarz (op. cit.) found evidence which indicated that such radiation effects resulted in a net reduction of iron, probably associated with a net increase in total iron, in the reactor zone rocks. They considered that the reduction of iron was most likely due to hydrogen produced by the radiolysis of water during nuclear criticality.

These effects were most apparent in those rocks in the immediate vicinity of the nuclear reactions; aureole rocks showed less extreme reduction characteristics. The addition of hydrogen, as the reduction mechanism, rather than the removal of oxygen, was favoured because the oxygen fugacity was considered much too low to facilitate oxygen removal.

The inventory of multivalent nuclear products in the Oklo reactor zones showed that 80% of the fission produced molybdenum, 35% of the technetium and 25% of the ruthenium were missing; small amounts of uranium had also been removed. As pointed out by Curtis and Gancarz (po. cit. p. 35):

> "To transport these elements from the rocks they had to be partitioned into the mobile aqueous phase. Each of them is multivalent, forming and insoluble oxide in the reduced tetravalent state. In higher oxidation states each forms a soluble oxyanion. These dissolved species are relatively mobile in the geologic environment because of the weak adsorption of negatively charged species on immobile phases. One apparently contradictory aspect of the geochemistry of these elements at Oklo is their mobility in what is overall an extremely reduced geologic environment. We suggest that this mobility reflects oxidation resonably occurred on the surface of uraninite grains. It has been proposed that fission products migrated to these surfaces by solid-state diffusion. In addition, some portion of these elements were "injected" into the fluid phase by fission recoil from the uraninite grains. Since the mineral host and the source of radioactive emissions were one and the same, fission products at the surface of the uraninite grain were literally immersed in radiolysis products."

As there is no evidence that these elements were deposited within the reactor zones, it is concluded that the aqueous phase active within these zones was sufficiently oxidising to retain these elements in solution. Depositional haloes of these elements took place outside the reactor zones, as reducing conditions were increasingly encountered.

In a comparison with the predicted radiation yield of hydrogen for the proposed Swedish radioactive wastes, Curtis and Gancarz (op. cit.) calculated the amount of radiolysis products/tonne of spent fuel in one of the natural Oklo reactors and found a remarkable similarity to the probable case, as predicted by Christensen and Bjorgbakke (1982).

5.6.2 Conclusions

The Oklo data provide excellent first-hand evidence that radiolysis of groundwater can occur in a waste repository and that it will have a marked, but very localised effect on the chemistry of the system. The chemical data are, however, rather ambiguous when it comes to assessing resultant redox conditions around a waste container. The following points can be made:

- radiolytic hydrogen gas did not behave inertly, but diffused into the clay mineral structure to reduce the iron present in these minerals. The apparent ready availability of iron and activity of hydrogen may have been enhanced by the elevated temperature and the open structure of the clays. However, the current KBS/NAGRA models assume the hydrogen to be inert and escape the system, thus tending to conservatively overestimate the extent of oxidation in the near field.
- although the Fe^{2+}/Fe^{3+} ratios in the reactor core zones indicate reducing conditions, the actual redox conditions are not known. The contradictory evidence of oxidising conditions necessary to mobilise some of the fission product elements seems to indicate that radiolytically induced redox conditions were very localised. For example although the fluid phase may have been oxidising at the surface of uraninite grains (sufficient to mobilise some fission products) and seems to have been buffered at a high enough oxygen fugacity to allow very small scale transport (a few metres) there was also sufficient hydrogen available to cause concurrent reduction of iron in the clays.
- the complex nature of the redox conditions in the near-field seems thus to preclude the simple notion of an oxidation front moving through the rock and mopping up all available reduced species whilst carrying radionuclides with it. Although this may be generally conservative, the reality seems to limit radiolytic redox reactions to the very near-field and to allow equal effect to the reducing power of hydrogen as to the role of the oxidants.

Some questions which thus require answering (both by laboratory and analogue study) are:

1. Did the localised transport of fission products from the oxidised uraninite surfaces actually take place in a reducing fluid, with the transport distance being controlled by the kinetics of their re-equilibration to these reducing conditions rather than by the position or even the existance of a distinct redox boundary?

2. Was the reducing capacity of hydrogen gas catalysed by surface effects on mineral grains, and by the high core zone temperatures? If only the latter, would hydrogen be as effective a reducing agent at the low temperatures of a repository?

5.7 Redox Equilibration

As discussed in more detail in the preceding section, radiolysis has been modelled as a near-field source of oxidants which could be transported for considerable distances along the flow path (around 50m in 10^6 years in a rock containing 0,2% Fe(II) - Neretnieks and Aslund, 1983a,b). Any such oxidant source is, however, considered to be buffered by remnant Fe or Fe(II) in corrosion products for the NAGRA case and it is calculated that any redox front would thus be contained within the bentonite barrier for at least 10^6 years (McKinley, 1984). There are several uncertainties associated with such models which may be elucidated by natural analogues:

1. The mechanism by which natural redox fronts are established and the behaviour of redox-sensitive species transported through such a front are very poorly understood.
2. The extent to which Fe(II) in minerals (and especially in intact granite) is available to buffer aqueous chemistry and the kinetics of such buffering have been little studied, especially in field situations.
3. The efficiency of iron oxy-hydroxides resulting from canister corrosion as redox buffers has not been quantified.

It should also be noted that, regardless of whether an oxidising near-field occurs or not, some redox front will occur along the flow-path at the transition between reducing, deep groundwater and more oxidising near-surface water. This zone has not been studied, as such, from an analogue point of view and hence, although not considered further in this section, will be discussed in chapter 6.

5.7.1 Analogues of redox equilibration

Natural analogues to study redox mechanisms should be relatively common considering that the majority of ore deposits, not least uranium, are formed when mineralising fluids gradually or suddenly encounter variations in temperature, pressure, pH, Eh, oxygen activity, etc. which prove to be conductive for precipitation. However, ore deposits are dominantly hydrothermal in origin and represent temperature ranges of 100°-500°C, mostly far in excess of the temperature conditions assumed (by KBS and NAGRA) to prevail around a breached canister (around 100oC).

Therefore, the most useful analogues will be those that can demonstrate (using strictly applied constraints of temperature, pH, Eh, $CO_3 2-$ etc.) naturally-occuring radionuclide mobilisation, transport and precipitation in a suitable homogeneous bedrock environment at lower temperatures (less than 100°C).

The redox behaviour of uranium has been extensively investigated and is relatively well understood in many natural occurrences of uranium mineralisation. Amongst the best documented cases are those hosted by sandstone-dominated sediments, the so-called roll front deposits (e.g. Adler, 1974; Granger and Warren, 1974; Rackley, 1976). These deposits are considered to be the product of a redox trap resulting from physical, chemical or microbiological processes. Hydrogen sulphide rich zones for example, precipitate ore minerals (U, V, As, Cd, Sc, etc.) from solutions on the basis of their over-saturation in solution which is sensitive to changes in Eh, pH and sulphide concentration. Deposition of these ores, therefore, is coupled to an oxidation reaction which may be reflected by an increasing amount of ferric iron at the expense of ferrous, a decreasing amount of mineral and organic carbon, and the conversion of pyrite to geothite and/or hematite. The decrease of organic material is often observed as a progressive change from vitreous, carbonised plant fragments retaining much of their original character (outside the influence of the roll front), to sooty but distinct masses (near the interface with the oxidised zone), to final obliteration (within the reduced zone). These reactions are often catalysed by anaerobic bacteria and effectively extend the reducing environment from its initial boundaries over a considerably larger area, thereby enhancing chemical exposure and reduction efficiency (Adler, 1974).

The main characteristic of these deposits is their spatial and genetic relation to irregular tongue-shaped zones of altered, oxidised rock, whose borders usually contrast sharply with the enclosing unaltered rock. The contact between the two rock-types is referred to as the redox interface and the part of the redox interface that curves across the host strata is called the roll-front. Such deposits, more accurately described as secondary uranium ore bodies, are the products of moving fronts (analogous to a radiolysis front) which are generated as groundwater moves through permeable zones from higher to lower hydraulic potential. Thus, roll fronts may be regarded as a migrating reaction zone between the aquifer rock and groundwater, where oxidising water reacts with reducing rock, with the result that both are changed. Isotopically, these changes are reflected in the fractionation of uranium and its daugther decay products. The nature and extent of this uranium-series disequilibrium has been discussed for ore deposits and their host sediments (e.g. Rosholt et al, 1965), and in general aquifer environment (e.g. Osmond et al, 1983).

These roll-front uranium deposits therefore hold great promise as active natural analogues for the redox situation envisaged surrounding a breached waste canister. In addition to providing evidence of a redox front, other useful data which can be obtained include:

a) the redox behaviour of uranium and its daughter products at ambient temperatures in the groundwaters and the ore/host rocks (using uranium-series disequilibrium measurements)

b) some idea of the geological time-scale for the migration speeds of these fronts (using isotopic constraints).

Redox conditions have also been examined at the Oklo natural reactor (Curtis and Gancarz, 1983). As described in Chapter 5.6, radiolytic oxidation within the reactor zones may result in increased partitioning of multivalent nuclides (e.g. Mo, Tc, Ru, U) into the aqueous phase and subsequent transport from the reactor zones to the surrounding sediments. On passing through a redox front precipitation could have occurred as the transporting fluids became increasingly reducing. Such precipitation could well explain the aureoles of nuclear products found in the sediments within ten metres from the reactor zones.

The transport of natural series radionuclides across a redox front is currently the topic of study in the Italian waste management programme. In this case the redox boundary is present in a thick sequence of pliocene clays overlain by tuffs at Orte, north of Rome. Oxidising groundwaters permeating down through the tuff and into fractures in the upper part of the medium-plasticity, blue clays have produced a red-coloured zone as iron and manganese within the clay were progressively oxidised. The redox front is a sharp feature situated a few millimetres either side of fractures in the clay. This study has only recently commenced, but by careful analysis of the redox state of Fe and Mn in the clays, the distribution of redox sensitive natural series radionuclides in the tuffs, clays and groundwaters, and by assessment of the hydrological regime during the last 60-100,000 years, it should be possible to examine:

a) the availability of iron within the clay for oxidation

b) the diffusion rate of oxygen from fissure-bound waters into the clay pore structure

c) the precise behaviour of natural series radionuclides as they diffuse across this redox boundary.

Uranium-series disequilibrium (i.e. in $^{234}U/^{238}U$ activity ratios) is a common feature of circulating groundwaters, and appears to be genetically related to the geological environment through which the waters permeate. Thus, $^{234}U/^{238}U$ disequilibria have been used to characterise water masses, to estimate degrees of mixing of different water masses, and as a means of dating groundwaters (e.g. Osmond et al, 1974; Kronfeld et al, 1975; Osmond and Cowart, 1976). The behaviour of natural series radionculides as groundwater traverses a redox front is well-documented from large scale aquifer systems (e.g. Kaufman et al, 1969; Osmond and Cowart, 1976; Cowart, 1980; Andrews and Kay, 1982). This has indicated that during the transition from an oxidising to a reducing environment, a decrease occurs in total dissolved uranium. This is generally accompanied by a decrease in Eh, pS^{2-}, O_2 and an increase in $^{234}U/^{238}U$ activity ratio due to excess ^{234}U (caused by recoil or "hot-atom" effects). Related studies have been carried out in groundwater flowing through or past mineralised uranium occurrences (Osmond et al, 1983; Airey et al, 1983, 1984) where uranium is mobilised by oxidising groundwaters and subsequently re-deposited down-stream as more reducing conditions are progressively encountered.

Of particular importance to the KBS and NAGRA programmes is groundwater redox behaviour in a crystalline bedrock environment. As stated above, existing models of uranium behaviour (Osmond and Cowart, 1976), are based on investigations carried out along large-scale sedimentary aquifers where the groundwater flow-paths and flow-rates are well-defined. Within a crystalline bedrock environment, however, groundwater flow is determined largely by the fracture pattern which is extremely difficult to interpret in three dimensions. Much more detailed study is required in these particular hydrogeological systems.

5.7.2 Conclusions

There is no doubt that changes in redox conditions within the near-field (KBS and NAGRA) and far-field (KBS) can greatly influence radionuclide migration. However, further data on some of the mechanisms which control these redox conditions around a breached canister would be particularly useful, especially as regards the kinetics and potential availability of Fe(II) in the host rock as an effective aqueous buffer.

Much information is already available from natural geological systems, and once again the Oklo analogue provides evidence for redox precipitation of fission products such as Mo, Tc and Ru. The geochemical and isotopic reactions across a redox front have been examined in some detail for sandstone uranium roll-front deposits. Direct application is, however, not always possible for envisaged near-field conditions because:

- sandstone represents a porous medium with hydraulic properties considerably at variance with the granite bedrock repository proposed by KBS and NAGRA
- the organic matter and microbial activity which can play a major role in establishing a distinct redox front will probably not be important at repository depths. The available organic material in the bentonite packing is conservatively estimated to be 200 mg/kg. Furthermore, groundwaters at such depths should be almost free of organic compounds
- there are large differences in the geometry of the redox front; redox front migration (KBS concept) in the far-field will depend on groundwater flow-paths along fractures in the granites and the extent of diffusion into the rock matrix.

On the more positive side, other redox-sensitive parameters investigated (i.e. Eh, pH, pS^{2-}, Fe^{2+}, etc.) across the roll fronts give us a much better insight into how these redox situations behave. In this respect, groundwater studies are playing an increasingly important role.

From the KBS and NAGRA points of view, uranium deposits hosted by granitoid rocks where uranium mobilisation occurs up-flow and re-deposition occurs down-flow (i.e. redox front conditions) would be a most suitable area for study.

5.8 Retardation during transport

During groundwater transport along the flow-path (or diffusion into the rock matrix - chapter 5.9), radionculides in solution will interact with available mineral surfaces by a number of physico-chemical processes. These can be categorised as:

1. physical (van der Waals) adsorption
2. ion exchange
3. chemisorption (reversible or irreversible)
4. ion exclusion
5. ultrafiltration

While the first 3 processes all involve uptake and could be evaluated in static systems (laboratory or field) it is important to note that the latter two are inherently dynamic and hence are very dependent on in-situ flow characteristics on a micro-scale.

Distinguishing between the mechanisms listed above is extremely difficult in a natural environment but the net result is observed as retardation of the solute relative to an ideal tracer to an extent which is dependent on both the element and the geochemical environment involved. Although a very extensive literature exists on laboratory measurements of such processes, extrapolation to the real environment has not been very well justified (discussed in detail by McKinley and Hadermann, 1984).

The requirements for an analogue study of retardation processes are:

i) a well defined source input function
ii) a well defined past hydrogeological environment
iii) a resultant measurable concentration profile.

Although generally classed as "natural" analogues, the source input could be either anthropogenic (for timescales up to about 1000 y) or arise from geochemical disequilibria (up to about 10^9 y). In general it can be expected that the accuracy with which an analogue system can be analysed will be inversely proportional to the timescale involved. The amount of geochemical data analysed in this context is relatively limited to date, but, potentially, data from a vast range of locations and processes could be utilised as analogues. The range of applications is large, and thus a number of examples, spanning a wide range of spatial and temporal scales, will be briefly described.

5.8.1 Natural analogues of radionculide migration

On the scale of 10^9 years the Oklo natural fission reactor has been widely studied, as the leachate from ore bodies in this region provides a reasonably well defined source input and elemental concentration profiles of mobilised species (or their deighters) can be measured in the surrounding rock (e.g. IAEA, 1975, 1978 and chapter 5.3). Although the source-term chemistry in this site might be expected to be similar to that resulting from the leaching of high level waste (especially for spent fuel disposal), quantitative analysis of this system is extremely complex due to uncertainties in the geochemical and hydrothermal histroy of the region. For this area, in fact, it is extremely difficult to separate the effects of solubility (or extent of leaching), speciation observed elemental profiles.

The results to date as summarised by Brookins (1984) are presented in Table 5 but it should be noted that the associated analysis of expected migration in terms of speciation/solubility (Brookins, 1978, 1984) is inherently very limited by uncertainties about the Eh/pH conditions experienced (e.g. Curtis and Gancarz, 1983) and the data-bases used for the thermodynamic speciation calculations, especially for the actinides (e.g. McKinley and Schweingruber, 1983).

For elements which have been predominantly retained in the reactor core regions it is impossible to distinguish mechanistically between source term (e.g. low solubility or leach-resistant matrix) or migration (e.g. very high sorption) effects. For mobile species, however, it may be possible to derive data on the relative retardation of different elements although without any indication of the causative mechanism. To select a single illustrative example, Gancarz et al. (1980) studied the distribution of Ru and Pb isotopes around the Oklo reactor zones and were able to show quite clearly that some mobilisation of ^{99}Tc (the parent of ^{99}Ru), Ru and Pb had occurred but that regions of deficiency and enrichment were separated by less than 10m. The migration of Tc and Ru occurred within approximately 10^6y of reactor criticality and hence the geochemical environment and flow conditions cannot be well defined while that of Pb has been continuous over about the last $1.8\text{x}10^9$ years but is limited by the source term (diffusive release from uranite). It would be very difficult to derive quantitative retardation data from either of these cases and such data could not be readily extrapolated to a relevant geochemical environment. Qualitatively, however, it does indicate that such species are unlikely to be very mobile in a reducing groundwater environment.

On a generally shorter timescale (around 10^6 years), the contact zone between igneous intrusive rocks and their host formations have been extensively investigated in an attempt to quantify the extent of elemental migration in these regions (e.g. Brookins, 1981b, 1984; Brookins et al., 1983; Laul and Papike, 1982, 1984; Wollenberg et al., 1984). In such work geochemical isotope techniques are used to date the intrusive event and, in some cases, may even allow rough evaluation of regional hydrothermal history. The dominant retardation processes occurring during such hydrothermal events (in the order of 200^o-300^oC or more), when extensive rock alteration and formation of secondary minerals may occur, and those relevant to flow under low temperature (less than 60^oC) conditions are probably totally different. As far as the KBS/NAGRA disposal concepts are concerned, therefore, such work is irrelevant as temperatures are always very much lower and in any case containment of waste throughout the "thermal" period is reasonably assured. For alternative disposal concepts in which high temperature migration may occur, it is probably more appropriate to consider the retardation reactions as secondary mineralisation of the type considered in section 5.5 rather than the low temperature processes discussed in this section.

Table 5: Element retention in the Oklo reaction zones
(after Brookins, 1984)

Element	Comments	Eh-pH Predictions	
		25°C	200°C
Krypton	Most migrated	Not applicable	Not applicable
Rubidium	Probable local redistribution	Not applicable	Not applicable
Strontium	Probable local redistribution	Not applicable	Not applicable
Yttrium	Most retained	Retention	Retention
Zirconium	Most retained: some local redistribution	Retention	Some migration
Niobium	Most retained	Retention	Retention
Molybdenum	Most migrated	Migration	Migration
Technetium	Local redistribution	Retention	Migration (?)
Ruthenium	Local redistribution	Retention	Minor migration
Rhodium	Most retained	Retention	Retention
Palladium	Most retained	Retention	Retention
Silver	Most retained	Retention	Retention
Cadmium	Most migrated	Migration	Migration
Indium	Most retained	Retention	Retention
Tin	Not yet studied	Retention	Retention
Antimony	Not yet studied	Possible migration	Some migration
Tellurium	Not yet studied	Retention	Retention
Iodine	Most migrated	Not applicable	Not applicable
Xenon	Most migrated	Not applicable	Not applicable
Caesium	Most migrated (?: perhaps locally)	Not applicable	Not applicable
Barium	Local redistribution	Not applicable	Not applicable
REE	Most retained	Retention	Retention
Lead	Variable migration	Retention or local redistribution	Some migration
Bismuth	Most retained	" " "	Some migration
Polonium	Most retained	Retention	Retention
Thorium	Most retained	Retention	Retention
Uranium	Some local redistribution	Retention or local redistribution	Some migration
Neptunium	Most retained	Retention	Retention
Plutonium	Most retained	Retention	Retention
Americium	Not measurable	Retention	Retention

The comments column indicates observed elemental behaviour. The other two columns indicate what the behaviour should have been based on predictions from Eh-pH information.

On yet shorter timescales (less than 10^6y) elemental profiles along groundwater flow paths may be analysed to examine natural retardation processes and convenient "source-terms" can be provided by ore bodies. For example, Airey et al. (1983) have reported detailed studies of the groundwater induced redistribution of uranium series nuclides within and down-gradient of uranium ore bodies in the Alligator Rivers region of the Northern Territory of Australia. A unique feature of uranium deposits is the presence of potentially measurable levels of the transuranics ^{237}Np, and ^{239}Pu and the fission products ^{99}Tc and ^{129}I which have developed over geological time. The current status of relevant studies in this project has been reported (Airey et al. 1983) as follows:

" (i) Mobilisation of radionuclides over geological time

Many of the ore bodies intersect the surface, and comprise weathered profiles overlying crystalline rock sequences. The radionuclides are mobilised by weathering and are redistributed throughout the resulting iron-bearing clays and quartz. A detailed mineralogical investigation of the weathering processes has been undertaken. An open system uranium model has been developed to describe the gross features of the analogue.

(ii) Groundwater induced transport of radionuclides - the role of colloids

Systematic studies have been made of the levels of uranium, thorium and radium isotopes in groundwater intersecting the deposits. Attempts are being made to include the fission products ^{129}I and ^{99}Tc and ^{36}Cl. Down-gradient of the Ranger One deposit, it has been possible to show that the uranium retardation factor is about 250.

Unlike uranium, a very substantial proportion of thorium is transported by colloids. The thorium isotopes do not appear to be in equilibrium with the solution. The implications to the prediction of the long-term migration rate are being evaluated.

(iii) The role of iron mineralogy in uranium, thorium and radium transport

Chemical techniques have been used to study the distribution of uranium, thorium and radium isotopes throughout the amorphous iron, the crystalline iron and the clay/quartz fractions of the weathered profile. Uranium and thorium concentrate in the iron phase; radium tends to associate with the clay/quartz. Since the crystalline iron, which is formed from the amorphous phase, is not readily accessible to groundwater, an additional mechanism for the retardation of uranium and thorium has been identified.

(iv) Time dependence of radionuclide sorption coefficients

Measurements have been made of the relative ratios of the parent-daughter couples ^{232}Th/^{288}Ra, ^{230}Th/^{266}Ra, ^{288}Th/^{224}Ra and ^{227}Th/^{223}Ra. Because of the very low levels of dissolved thorium, the data set is not complete. Nevertheless, attempts are being made to interpret systematic differences in terms of the time dependence of distribution coefficients."

Some additional work based on the Th deposits at Morro do Ferro (section 5.4) has been reported (Eisenbud et al., 1982a, b, 1984) in which the distribution of Th between groundwaters, soil and sediment has been examined. While the generally low mobility of Th and the importance of organic components in enhancing its mobilisation are qualitatively demonstrated, quantitative extrapolation from the surface environment considered to relevant deep groundwater conditions would be impossible.

Even in the absence of distinct "source zones", profiles of natural series radionculides may be used to assess the rate of natural migration processes, but in most cases, for example in the consideration of rock weathering profiles (e.g. Michel, 1984), it is extremely difficult to separate control by release as opposed to retardation processes, even at a qualitative level. In a study of the Carrizo aquifer in Texas, in which flow occurs in sand bounded by well defined aquitards (Fröhlich et al., 1980; Pearson et al., 1983; Andrews and Pearson, 1984) waterflow rates were derived from ^{14}C data which allowed ^{234}U/^{238}U ratios to be interpreted in terms of the extent of U retardation. Using a very simple model which assumed all retardation can be measuring by a "linear" sorption isotherm, a "Kd" for U in this system of 6 (g/g) was derived from field data.

Even in cases where the flow conditions are not particularly well defined, retardation data can be derived by simultaneously measuring a large number of natural series isotopes in water samples (e.g. Krishnaswami et al., 1982; Hubbard et al., 1984). In the former study, indeed, not only were retardation factors for Ra, Th and Pb evaluated (ranging from 4500 - 200,000) but also very fast kinetics were inferred for the sorption reactions involved. It may be noted that the spatial scale of such studies can range from that of major aquifers, as considered above, to migration within and around single mineral grains (e.g. Rama and Moore, 1984) but the latter part of this spectrum will be considered in more detail in the following section on matrix diffusion.

More qualitative information, which is neverthless extremely useful, can be derived from a wider range of natural series studies. Hussain and Krishnaswami (1982), for example, use measured activities of ^{214}Pb, ^{212}Pb and ^{222}Rn in deep groundwater not only to show very fast removal of Pb from these waters but also to indicate the similarity of geochemical behaviour of Pb and Th under in-situ conditions. As an alternative approach, King et al. (1982) used ^{222}Rn/^{226}Ra activity ratios in different aquifers to assess the relative retention of Ra in each.

It should be noted that in such "natural series" based on geochemical studies it is also possible to concentrate analysis on the solid phase which may distinguish between sorption and retardation process (cf. McKinley and Hadermann, 1984). Very little work on this topic has been reported to date however, and that which has involves rather speculative interpretation of "recoil" enrichment of depletion processes which renders such results qualitative at best (e.g. Rosholt, 1980; Shirvington, 1980, 1983).

In addition to retardation during flow, analogues for the processes occurring during diffusive transport of solutes through the bentonite buffer are required. Although a considerable volume of geochemical studies of element redistribution in modern sediments have been reported, the large effects of bioturbations (e.g. Guinasso and Schink, 1975) or complex chemical profiles (in terms of Eh, pH, carbonate, etc. - e.g. Colley et al., 1984) generally preclude their use as clay buffer analogues. Some attempts have been made, however, to analyse natural series profiles in marine sediment as analogues for migration (particularly in a "sea-disposal" context) but the models used for data interpretation have, to date, tended to be somewhat simplistic (e.g. Laul et al., 1981). One study which may be useful in this context, however, is that based on analysis of the sediments of Loch Lomond in Scotland where a "source term" is provided by a band of marine sediment interbedded between lacustrine material as a consequence of the Flandrian marine transgression about 6,000 years ago. From a study of the profiles of 20 elements and natural series nuclides (MacKenzie et al., 1983; McKinley et al., 1984a) it was concluded that:

"a) Refractory species, Al, Si and La show sharp variations in concentration with depth and Al, As and Mn show greatly enhanced concentrations in narrow bands corresponding to the fresh/marine boundaries (presumably reflecting brackish conditions) all of which indicates that physical disruption of the sediment profile (e.g. by bioturbation) has been negligible.

b) I and Br are highly concentrated within the marine band with no evidence of post-depositional mobility.

c) Expected increased concentrations of Na and Cs in the marine band are not observed implying relatively rapid redistribution of these species.

d) Ce, Eu, La, Sm, U and Ra show similar profiles in which concentration decreases with distance from the marine layer which could represent levels of mobility intermediate between b) and c) above."

By use of a simple model, diffusion coefficients (or retardation factors) have been calculated from profiles of the type described in d) above (MacKenzie et al., 1983).

On yet shorter timescales, anthropogenic releases can be used to study migration processes, but the little work done on such tracers in relevant groundwaters has tended to concentrate on species which are assumed to be unretarded and hence can act as indicators of recent meteoric water (e.g. ^3H and ^{137}Cs from bomb fallout, pesticides, etc.). As an analogue of direct groundwater releases, radionuclide profiles resulting from underground nuclear weapons tests have been studied (e.g. Hoffmann et al., 1977; Hoffmann, 1979) but the complex source term and the degree of perturbation of both chemical and hydrological systems by the nuclear blast greatly limit the extent and applicability of data produced.

All of the examples quoted above, both qualitative and quantitative, are inherently suitable only for testing against models using laboratory data and any "retardation" or "sorption" data derived directly from these or similar projects must be viewed with great caution. Only in very short-term analogue studies, predominantly involving anthorpogenic source terms, can the three requirements listed at the beginning of this section be specified in sufficient datail to allow realistic back-calculation of retardation data.

An extensive literature exists of measurements of both "bomb fallout" and nuclear industry released radionuclides in soils and recent marine and lacustrine sediments (e.g. Coughtry and Thorne, 1982a,b; Coughtrey et al., 1983). In such work partition coefficients (or Kds) are often reported which are the ratio of elemental concentration (or activity) in the solid phase to that in solution which are directly comparable with laboratory measured "batch sorption" values. This data base is obviously a very useful benchmark for checking laboratory measurements against but the data cannot be directly extrapolated to a relevant deep groundwater environment due to the large differences in water chemistry involved (in particular Eh, pH and dissolved organic carbon) and the dominant geochemical role of micro-organisms in such near-surface environments (e.g. Jakubic, 1979; Jakubic and Kahl, 1982).

5.8.2 Conclusions

1. As far as retardation processes relevant to KBS/NAGRA are concerned, only rather vague, qualitative data have been obtained from studies of Oklo while studies of high temperature (e.g. igneous intrusion) systems are irrelevant. For disposal concepts in which high temperature migration is feasible, retardation is probably best considered in terms of secondary mineralisation processes.

2. Studies of groundwater flow around ore bodies have produced a fair amount of qualitative data on site-specific migration which recent developments in modelling approaches are allowing to become increasingly quantitative. More generally, rock weathering profiles or aquifer transects can be studied using a multiple natural series isotope approach which can allow quantification of both the extent and the kinetics of retardation.

3. Sediment profiles containing distinct and dateable geochemical anomalies appear to have great potential in quantifying the extent of retardation during solute diffusion through clay.

4. From measured concentrations of analogue elements (particularly anthropogenic radionuclides) in both rock and solution phases, partition coefficients can be calculated which can be compared to laboratory measured values. Unfortunately, such data are mainly restricted to a near-surface environment and cannot be readily extrapolated to a relevant deep groundwater system.

5.9 Matrix Diffusion

Far-field radionuclide diffusion into a water-saturated rock matrix, even in such dense crystalline rocks as granite, is considered to be an important factor in radionuclide retardation (Neretnieks, 1980; Rasmuson and Neretnieks, 1981; Hadermann and Rösel, 1984). Section 5.8 has outlined fluid-flow retardation mechanisms such as reversible and irreversible sorption of radionuclides into fracture and fissure mineral coating phases. In addition to fluid-flow retardation effects, radionuclides dissolved in the groundwaters could diffuse through the fracture surface coatings (presumed at this stage to be saturated to roughly a constant concentration from sorption processes) into altered and more porous (or even intact) areas of crystalline bedrock, by way of a continuous pore system consisting of microfissures between crystals in the rock matrix. Diffusivity of the radionuclides will depend to a large extent on their sorption properties. Poorly sorbing radionculides (e.g. ^{129}I) will be expected to penetrate far into the matrix while sorbing species (e.g. ^{237}Np and ^{238}U) may be strongly retarded. The former are thus expected to saturate the rock sections between the fractures (for the timescales considered for safety analyses), whilst the latter, after millions of years, are expected to achieve penetration depths of only some tens of mm.

In effect, as the groundwater flow in the bedrock will be in fractures and fissures spaced fairly far apart (up to tens of metres), the diffusion of radionuclides into the rock matrix from the fissures may be the main retarding mechanism, thus making the rock nearest the fracture a powerful "sink" for the nuclides. This approach has been adopted in the recent KBS safety analyses. The implications of the matrix diffusion model were aptly summarised by Neretnieks (1980, p. 4394):

> "The possible diffusion into the rock matrix has very important implications on the transport of radionuclides from a final repository. If it can be proved beyond doubt that this mechanism is active and that the diffusivities are of the magnitude used here, then a few hundred metres of good rock will be a most effective barrier for most of the radionuclides of importance in spent nuclear fuel. The diffusivity must, however, be validated, and not only for the times and distances which can be handled in a laboratory but also by using geologic evidence for migration of ions."

Laboratory experiments have demonstrated that matrix diffusion of ions occurs through samples of limestone (e.g. Garrels et al., 1949) and sandstone (e.g. Klinkenberg, 1951). Although characterized by different physico-chemical properties, samples of granite also appear to be conducive to micropore diffusion processes (Skagius and Neretnieks, 1982, 1983; Torstenfelt et al., 1982b; Birgersson and Neretnieks, 1982, 1983). To date it is felt reasonable to conclude that the laboratory-oriented studies indicate the matrix diffusion takes place.

Because the phenomenon of matrix diffusion has only recently been considered, continued efforts are in progress to further improve the laboratory-based experiments and provide additional quantitative data. There are, however, several factors which make supporting natural analogue validation particularly important:

1. **Time scale:** normally days to years under laboratory conditions as compared to more than 10^7 years for the repository concept. Laboratory data record radionculide penetration to depths of a few mm, which could be due to marginal mechanical stresses (resulting in enhanced porosity) from the sampling procedure (discussed under point 2). Laboratory timescales of greater duration are thus desirable in order to obtain diffusion profiles penetrating to depths considerably deeper than any marginal effects which might have been produced as a result of sampling and sample preparation procedures.

2. **Sampling:** samples for laboratory studies require selection from compact granite at realistic depths (i.e. 500-1500m). Samples have either been taken from drillcores, or overcored portions from larger samples. In both cases the mechanical drilling (under high hydraulic pressure) or overcoring methods may have induced marginal stresses, which could result in enhanced diffusivity within the outer skin of the sample. Furthermore, internal stresses are modified as the specimen is removed from depth (high overburden pressure) to the surface. These problems have been recognised and experiments have recently been carried out at depth in "undisturbed" rock in its natural stress environment (Birgersson and Neretnieks, 1983). Diffusion experiments were interpreted as showing "that all three tracers (Cr-EDTA, Uranine and I^-) have passed the zone disturbed by the presence of the injection hole and migrated into 'undisturbed' rock". Average diffusivities were found to be comparable to those obtained in laboratory experiments. Large variations in penetration depth (up to 20cm) were detected and further work is in hand to examine the mechanisms involved, including much longer timescale experiments.

3. **Fluid Phase:** the problem exists of simulating, under laboratory conditions, the physico-chemical properties of the groundwaters encountered at realistic depths in the granite.

In summary, the concept of matrix diffusion is attractive and would have very important implications on the far-field transport of radionuclides. At best it can be an effective delay mechanism for unsorbed radionculides as well as making available a larger rock surface area for sorption. However, more information would be desirable from natural analogues to answer several important questions which have been identified from the laboratory and field experiments:

- is there a connected structure of open and waterfilled microfractures in the intact rock matrix into which radionuclides can diffuse tens of cm (sorbing nuclides such as ^{237}Np and ^{238}U) or metres and even perhaps tens of metres (non-sorbing nuclides such as ^{129}I)?
- is penetration into the rock matrix restricted to a limited weathered (or otherwise altered or physically weakened) zone marginal to the water-conducting fracture?
- will the connected micropores observed in laboratory studies change their porosities owing to physico-chemical processes over very long times?

There may also be other processes, as yet unidentified, which may be active over long timescales.

5.9.1 Matrix diffusion analogues

As with the laborarory studies, suitable analogue studies of matrix diffusion are often limited by the difficulties of obtaining suitable samples. For example, a possible analogue test for matrix diffusion effects at low temperatures is to sample a rock profile which intersects a water-conducting fracture zone known to be transporting measurable amounts of uranium (i.e. with a radionuclide source). Diffusion of uranium, through the fracture coating layer into the host rock, should establish a diffusion profile. However, it is rarely the case in nature that the fracture zone will represent a "clean break" from which measurements will conveniently reveal a diffusion profile into the host rock. The fractures are likely to be the result of movement in the rock by tectonic stress, and zones marginal to the major fractures will often be characterised by secondary minor fractures and systems of hair-line microfractures.

Such minor structures might effectively enhance the porosity and have a major effect on the calculated extent of matrix diffusion. This enhanced porosity in turn increases the extent of penetration of low temperature alteration or weathering processes and, in all probability, facilitates the eventual movement of radionculides into the host rock.

Prior to assessing migration processes in this particular situation, it is critical to know the maximum extent of enhanced porosity and permeability due to the tectonic and geochemical (i.e. deuteric/hydrothermal/weathering) history of the fracture zone and the host rock.

Analogue studies of the type discussed above are presently being carried out by Cramer and Gascoyne (pers. comm. 1984) in the Lac du Bonnet batholith, Manitoba, and by KBS and NAGRA as a joint venture studying drillcore samples of granite and gneiss selected from test-site areas in Sweden and Switzerland.

Cramer and Gascoyne are studying element mobilities and mass transport processes in a granitic host-rock matrix along distinct water-conducting fractures. Sampled profiles (1cm thick slices) extending from the altered fracture surface into the unaltered granite have been analysed for major and trace elements, and both stable (^{18}O) and radioactive isotopes (uranium-series).

Preliminary results indicate that the alteration zone bordering the fracture penetrates some 3cm into the granite, and that it has been possible to distinguish, on the basis of the major and trace element chemistries, the effects of the early deuteric/hydrothermal alteration from the more recent low temperature weathering influences.

This is an important distinction as it is the low temperature processes which are of major importance in far-field considerations. Within this complex alteration zone, uranium shows increases from the unaltered granite (2-3 ppm U) to the fracture surface (about 15 ppm U): in some samples there is a decrease in uranium just at the fracture surface. Thorium concentrations (5-15 ppm) do not show any clear trends. In contrast, $^{234}U/^{238}U$ activity ratios decrease to a minimum about 1cm from the fracture surface, before returning close to equilibrium for the surface samples.

The uranium enrichment is considered coeval with the late-stage deuteric or later hydrothermal processes associated with the history of the granite. The decrease in activity ratios is attributed to the recent leaching of uranium (last 1-2 million years), and the return to almost secular equilibrium near the fracture surface suggests some kind of chemical or physical equilibrium with the groundwater due to the redeposition of ^{234}U onto surface grains. In terms of possible matrix diffusion considerations, these results are interesting in that:

- alteration/uranium enrichment along fractures at temperatures ranging from 100^{o}-800^{o}C (deuteric/hydrothermal) have apparently only influenced a zone some 3cm in extent into the host granite.
- more recent low temperature weathering effects have been confined to this 3cm zone with removal of uranium (reverse diffusion profile?) limited to a 1cm zone immediately adjacent to the fracture surface.

Further analytical results from this study, especially when viewed together with the microfabric characteristics of the unaltered granite/deuteric-hydrothermal/recent weathering zones, should prove to be most interesting.

Analogue studies to test matrix diffusion effects marginal to hydrothermal vein deposits, have been carried out by Shea (1984), Smellie (1982) and Smellie and Rosholt (1984). Using mainly fission track mapping techniques, Shea (op. cit.) has investigated the movement of uranium from a hydrothermal vein deposit into the country rock consisting of a quartz monzonite/monzonite and granite. Uranium sites studied included veins and veinlets, microcracks, secondary minerals, sealing microcracks, rock matrix, grain boundaries and cleavages and accessory minerals.

Uranium distributions were analysed along eight profiles from the mineralised vein into the host rock. Of these, two showed evidence of uranium diffusion (1cm and 5cm penetration respectively), two showed limited diffusion, one indicated a more complex history, and three showed no evidence of uranium diffusion. Derivation of the apparent diffusivity values for the rock matrix (Da) and distribution constant values (Kd) indicated that the retention in these granitic rocks was orders of magnitude greater than expected from laboratory considerations. This was attributed to greater amounts of microfracturing, secondary mineral formation within macrocracks, time and temperature dependence of Kd, oxidation state of uranium, and preferential sorption/reduction by chlorite and pyrite.

Alternatively, we consider that if the laboratory values of Kd are in fact approximately correct, then the values of diffusivity must be much lower than are used in matrix diffusion calculations. Although this compensates for the limited diffusion observed by Shea, it may indicate that matrix diffusion is in fact much less efficient than has been suggested.

Because of the nature of this deposit, i.e. mineralising fluids at about 150°C introduced along brecciated structures in the granitoid complex, it is not surprising that these mineralising fluids have preferentially penetrated the rock matrix by way of macro- and microstructures. Along some of these subsidiary veinlets and microfracture infillings, some diffusion (at least in two dimensions) of uranium into the country rock appears to have occurred, but only to a very limited extent. Because of the limitations of the fission-track method, the nature of this uranium (primary hydrothermal vs. remobilised secondary) is unknown. Some uranium-series disequilibrium measurements should prove to be very useful in this respect. In general, this study demonstrates, as emphasised by Shea (op. cit.), the retentive properties of the host granitoids, rather than demonstrating convincingly that matrix diffusion occurs.

Similar retentive properties have been observed from many of the granites and metavolcanics of N. Sweden which host Proterozoic hydrothermal uranium vein deposits (Halenius and Smellie, 1984). Lateral movement of uranium into the country rocks, usually present as interstitial disseminations of fine uraninite grains, is mostly restricted to a border zone 1-5cm wide, immediately adjacent to the main mineralised fractures. Greater penetrative depths are usually associated with minor fractures and networks of microfractures. Smellie (1982) and Smellie and Rosholt (1984) have studied radioactive disequilibria measured along profiles from the mineralised veins into the country rock.

Three hydrothermal veins were investigated from two areas, one hosted by metavolcanic (rhyolitic in composition) and two hosted by a leucocratic granite. Most of the samples measured indicated radioactive disequilibrium; in general the highly mineralised samples (i.e. the vein uraninites) were depleted in ^{234}U and the weakly mineralised samples, located adjacent to the former, contained excess ^{234}U.

The limited data therefore suggest that during the last 0.5Ma, weakly mineralised samples at depths of 55-130m have been picking up ^{234}U nuclides from the surrounding pore fluid and may still be doing so. Whilst the study shows the behaviour of the uranium daughter nuclides resulting from rock-water interaction under reducing conditions (no isotopic evidence of bulk oxidative leaching of ^{238}U), and these nuclides have undoubtedly moved out of the mineralised zones into the adjacent country rock, migration is considered to be controlled by fine, interconnected networks of microfractures, revealed from petrofabric studies of the analysed samples. Furthermore, migration of nuclides in fractures and microfractures orientated parallel to the mineralised veins, derived from mineralised areas at shallower or greater depths, cannot be ruled out.

5.9.2 Conclusions

In conclusion, the concept of matrix diffusion is attractive and would have very important implications on the far-field transport of radionculides as well as making available a large rock surface area for sorption. Its importance is reflected in the attention it is receiving in the respective safety assessment programmes of NAGRA and KBS. To date, however, neither laborarory nor analogue studies have provided conclusive evidence of the magnitude of the process or resolved all the mechanisms involved, although identifying the most important parameters for further study. Further in-situ tracer experiments would clearly be valuable in this context. The major difficulties to be surmounted are the time-scale factor (experimental studies) and the suitability of the samples to be investigated which is a problem shared by both laboratory and analogue study programmes. Because predicted diffusion of radionculides into intact rock may only be in the region of a few mm (with regard to sorbing species), it is critical that near-surface mechanical and chemical effects on samples, which may result in enhanced porosities and permeabilities, be fully assessed before any definitive interpretation of matrix diffusion is attempted.

6. SCOPE FOR FURTHER STUDIES

From the analysis of existing work on natural analogues presented in the previous Chapter, it is apparent that many opportunities exist to expand these studies or, indeed, to develop novel analogue approaches. These possibilities for further studies are considered below for each of the processes considered in Chapter 5 while, in the next Chapter, the requirements and priorities of safety assessment modellers (cf. section 3.2.1) will be used to identify key research areas.

6.1 Long-Term Stability of Buffers and Seals

It would appear from section 5.1 that kinetic studies of analogues for illitisation of the bentonite buffer are fairly complete and little further work on this aspect would be required. Direct thermal effects on the properties of bentonite in terms of their variation with distance away from a heat source have not been considered in much detail and further studies of igneous intrusions into relevant clay formations may be useful. The prime aim of such work would not be examination of the chemical control of illitisation, which seems to be quite well-established, but rather study of the effects of the transformation between clays on the physical properties of the clay body (e.g. swelling properties, resistance to particulate transport, hydraulic conductivity, etc.). It is thought quite likely that illitisation of the backfill might not, in any case, significantly alter its essential properties as a buffer.

One further chemical consideration which might be amenable to analogue studies is the direct hydrothermal interaction between canister and backfill. High temperature laboratory studies indicate that, for example, metal silicates may form at the canister/bentonite interface but there has been no quantitative analysis of this process. It may be possible to identify locations in which ore bodies are adjacent to relevant clay formations which would provide useful elucidation of the relevant importance of this reaction.

6.2 Waste Package Corrosion

Analogue studies of the stability of native copper deposits provide important justification for the long canister life-times modelled by KBS. The case for copper stability in relevant groundwater has been well demonstrated but a requirement exists for a comparable study of iron.

Localities of iron corrosion under relevant geochemical conditions are more limited but, for example, native iron deposits in Greenland might be considered. Of less immediate importance, but worth considering in the long-term, is the effect of "unlikely events" on canister corrosion. A "worst case" for the repository concepts involved might be a change of groundwater chemistry (by some drastic event) to become more oxidising and hence more aggressively corrosive. The consequence of such an event might be investigated by studying Cu and Fe mobilisation in the vicinity of mines in relevant formations where the mining process itself has perturbed the natural groundwater redox system.

Archaeological analogues of metal corrosion were found to be very useful and allow at least semi-quantitative determination of rate of corrosion in various geochemical environments. The consistency between the results of different studies was surprisingly good and would appear to merit more detailed analysis of particular artefacts (e.g. to study pitting factors for iron in more detail). As with all the chemical processes considered, extrapolation of data between different geochemical environments is extremely difficult and any future work should concentrate on artefacts exposed to reducing groundwater of reasonably similar chemistry to that expected (e.g. Fe and Cu artefacts found in old wells and abandoned mines).

6.3 Waste Form Breakdown

The difficulty of extrapolating data from natural glasses to vitrified high level waste was discussed in section 5.3 and would seem to indicate that further chemical studies of such analogues would be unproductive. One factor which is of great importance for safety calculations, however, is the extent to which the vitrified waste block will be fractured at the time of canister failure as the waste leach rate and alpha/beta radiolysis rate are directly dependent on the available surface area.

A useful analogue of this long-term fracturing process, which is inherently very difficult (if not impossible) to study in the laboratory, might be found in massive occurrences of natural glasses. By studying the age and mechanical properties of such glasses in relation to the observed degree of fracturing, some quantification of this process may be possible. In addition, if the hydration profiles around such fissures and the overall hydrologic properties of the glass mass are evaluated, data may be provided which could greatly improve the realism of present conceptual models of glass leaching.

For spent fuel, Oklo seems to be the ideal analogue and it would seem possible that more useful information could be derived from this source. For example, micro-scale analysis of the inter-crystalline phases which had contained actinides and fission products may improve understanding of the structure of spent fuel (which has been relatively poorly studied) and may improve mechanistic modelling of the leaching of this material form in Oklo and other high grade uranium deposits. Measurement of the extent of loss of rare earth elements during such metamictisation would also be useful in this regard.

6.4 Solubility and Speciation

Direct extrapolation of solubility and speciation data between different geochemical environments is almost impossible and, except for very general evaluation of equilibrium thermodynamic models, future work should be focused on relevant groundwater systems. Well defined elemental sources, for example ore bodies such as Morro do Ferro, or mill tailings, can be very useful in this regard as long as analysis is focussed on deep groundwater systems. Extensive analysis of speciation both in interesting source regions and in potential host rock are critical to the validation of the thermodynamic models used in safety assessment but the greatest practical limitation on such work is probably sampling of deep groundwater. The perturbations involved in current sampling methodologies for crystalline groundwater are well known (e.g. contamination by drill-water, air and microbes, degassing, unrepresentative sampling, etc.) and the techniques have to be improved.

6.5 Mineralogical Fixation at Elevated Temperatures

From section 5.5 it is apparent that most of the analogue studies of this topic involve temperatures which are too high to be relevant to either the NAGRA or KBS disposal concepts. Although of little direct relevance, the secondary mineralisation around late stage hydrothermal vein systems may need to be studied to allow this process to be decoupled from other analogue processes which may be of much more direct relevance (e.g. matrix diffusion - section 5.9). Such analysis could include examination of existing low-temperature geothermal systems and surface weathering profiles which would also yield some kinetic data but, in most cases, such data could be reliably derived (much more cheaply) from laboratory measurements.

The main use of any such analogue work would be to validate the results of thermodynamic models based on background laboratory data and thus, to increase its relevance, should be based in a location with appropriate groundwater chemistry (in terms of Eh, pH, organics, etc.).

6.6 Radiolysis

The open questions raised in the radiolysis section (5.6) are probably best examined by laboratory-based rather than analogue studies. The apparent disagreement between modelled and observed near-field redox conditions is, however, very important. Thus, after a better understanding of the basic processes occurring in groundwater radiolysis in relevant conditions has been derived from laboratory studies, a further more detailed examination of the Oklo reactor sites may be warranted. The main problem with the analogue studies to date is that they have been based on a single location. If any other natural reactor sites could be identified (e.g. by isotopic analysis of commercial U mineral samples), a study of the resultant radiolysis profiles would be extremely useful.

6.7 Redox Equilibrium

Although the reality of an oxidising near-field seems uncertain in the light of the Oklo analogue discussed in section 5.6, there is a requirement at present to model redox buffering reactions which can be examined by many natural analogue systems.

For the NAGRA case, radiolytic oxidants will be buffered by canister corrosion products and the kinetics and general efficiency of such buffering could be investigated at locations where native iron (e.g. Greenland), iron ore (e.g. Kiruna) or massive magnetite (e.g. Morro do Ferro) were present in a relevant groundwater environment. For the KBS case, the redox front penetrates the backfill and gradually moves through the host rock. In the calculations involved, the buffering effect of the bentonite itself is ignored but this could be examined by analysis of redox fronts (e.g. Orte study) or small scale reduction spots ("birds-eye" features) in natural clays. Buffering by the rock mass is modelled to involve diffusive transport of oxidants into the rock matrix where they react with Fe(II) containing minerals. These processes could be examined in any natural or artificial (e.g. geothermal) fissures in which oxidising water has been flowing for a known time period.

In such analogue studies it is very important that the rock formation studied be similar to the envisaged host rock. The diffusion and iron-oxidation processes could, however, be decoupled by investigating the extent of oxidation of Fe(II) in relevant minerals exposed to flowing oxidising water for a known time period (e.g. analysis of surface minerals exposed to flowing water since a known period of glaciation). Although not present in current KBS/NAGRA concepts, it should be noted that specific redox buffer species can be added to the bentonite backfill and their efficiency can be assessed by analogue studies (e.g. pilot study of graphite at Athabasca - J.Cramer, pers. comm.). A theoretical and experimental study of this option has been made by Hannerz and Hyden (1978).

Apart from the formation of a redox front, the mechanisms by which solute transport may be accelerated (e.g. by colloid formation) or retarded (e.g. by precipitation) at such fronts is very important. As yet, this topic has not been studied but valuable data might be obtained by microscale analysis of chemistry, mineralogy and particulates along profiles through the redox front at any of the analogue locations previously considered.

6.8 Retardation During Transport

Although much analogue information on elemental sorption and retardation has been reported from a wide range of environments, very little is directly relevant to the NAGRA/KBS concepts. Future analogue work should be located in relevant geochemical conditions and several "ideal" situations could be envisaged:

1. Where a water-carrying fissure is cut by a distinct vein with very high concentration of natural series radionuclides. Preferential leaching of daughters should result in downstream profiles of a number of nuclides (e.g. ^{234}U, ^{226}Ra, ^{210}Pb, etc.) which, in a steady state, would be dependent on their half-life and degree of retardation. Such work could also be extended to examine profiles of nuclides into the intact rock resulting from matrix diffusion.

2. Where anthropogenic waste has been disposed of in a relevant rock. A typical example might be where waste arising from ore processing has been dumped in an old mine or shaft at a time which is historically or archaeologically datable. Coupling of measurements of source input, water flow and resultant migration profile would yield retardation data directly. Again, such a location would be suitable for matrix diffusion studies.

3. Where well defined sedimentary structures exist. Retardation in the bentonite barrier must also be quantified and existing studies in which elemental profiles resulting from diffusive transport from well defined (and dated) elemental discontinuities seem to form appropriate analogues. Locations should be selected in which clay mineralogy, physical properties (e.g. porosity permeability) and water chemistry are as similar as possible to those in the repository.

4. Where flow occurs in large scale "lineaments" in a relevant rock formation. For the KBS concept, in particular, the last stage of "far-field" transport to the surface occurs in large scale regional faults (lineaments). These might be studied using the natural series/stable isotope approach, to date applied only to aquifers.

In all the above examples full chemical characterisation of the groundwater involved is essential in order to assess the magnitude of extrapolation involved in relating data produced to the actual repository environment.

6.9 Matrix Diffusion

The usefulness of information from analogue studies of matrix diffusion has, to date, been limited by (a) unsuitably high temperatures which prevent immobilisation by secondary mineral formation being distinguishable from very low diffusion rates and/or (b) inapplicable rock type or water geochemistry. Ideal analogues for examining this process have already been considered in section 6.7 (redox front penetration into rock matrix) and 6.8 (studies 1. and 2.) which would allow measurement of the effective diffusivity of a number of elements into the rock. For the natural series experiment (study 1. section 6.8) in particular, it may be possible to examine migration of different isotopes of the same element (e.g. ^{226}Ra, ^{228}Ra) which, by examination of different timescales, may show up any change in "diffusivity" with distance from the fissure which micht be expected due to more extensive microcracking in the vicinity of the main fissure.

One further analogue for matrix diffusion which could be very useful involves fissures which have been subjected to inflow of saline water over a well defined period where chloride may act as a very good tracer to quantify the inherent diffusivity of the rock.

7. CONCLUSIONS

Natural analogues have undoubted potential in answering some of the more intractable questions regarding the very long term predictability of processes in the natural environment. To date they have been used in a rather piecemeal fashion where information was obviously available, and, in many cases, they have been applied on rather too broad a scale with the result that they are open to criticism regarding their applicability. More recently, "analoguing" has been applied to specific problems with limited and tightly defined objectives, with considerably more success in terms of the usefulness of the data.

This highlights what we regards as perhaps the central principle of natural analogue use; it is not possible to find an exact (and hence unimpeachable) counterpart in nature to the behaviour of the whole, or even any major part of, a deep waste repository. Their fundamental use, indeed the area where they may provide the only valid means of control, is in the verification of specific processes which can be decoupled for reliable observation. Their use may be as milestones or benchmarks to quantitatively control the result of a model, or as signposts to ensure that a model or prediction is going in the right direction. They are unlikely in themselves ever to be useful for the construction of models, and would appear to be much more useful when chosen to control existing laboratory or model data, rather than the other way round. In this way very careful selection to remove uncertainties or inappropriate environments, time scales, etc. allows optimum use of the technique. It is in this selection process that we detect a communication gap between analogue users and earth scientists, who hold in store a wealth of useful but untapped information. We hope that by outlining here in some detail the processes which require analogue support and the rather exacting requirements of a good analogue, geologists unfamiliar with radwaste studies will be able to help identify specific sites, localities or instances which offer new potential for the modellers. In this respect we feel that greater access to data from the uranium mining industry would be very helpful. There is a clear need to co-operate more and co-ordinate better. Problems of poor sample availability and especially of inadequate techniques for both fluid and solid sampling could be more easily resolved if a greater number of well co-ordinated joint projects were underway. This would also help to breakdown the frequently observed communication barrier between radwaste modellers and the geologists.

Our review of available analogues has shown that almost all of the useful information relates to chemical processes. Several purely physical processes, some of great importance to systems modelling, appear not to be amenable to analogue study. These are processes involving groundwater flow where observations can only really be made on the same time scale as the process one is trying to extrapolate by analogy. Among these are assessment of regional groundwater flow, and prediction of the long-term hydraulic properties of seal bonds.

The review also highlighted the lack of good analogues in the time range of 1,000-100,000 years; that is between archaeological analogues and the bulk of geological analogues where timescales of 10^6-10^7 years are those most commonly considered.

Apart from these general observations a number of specific conclusions have been reached regarding the application of existing and potential analogues to the NAGRA/KBS concepts. These are listed below, although in no particular order of significance:

7.1 Conclusions Drawn from available Analogues

1. Transformation of the bentonite buffer material to illite in a granite repository with consequent degradation of hydraulic properties is likely to take at least 10 million years. Even then hydraulic properties may remain adequate. The scale of any thermal effects on clay physical properties (for the NAGRA higher temperature concept) will be limited to a few tens of centimetres at most.

2. Archaeological analogues for copper and iron corrosion rates are surprisingly consistent and give estimated times for purely corrosive canister penetration of about 250,000 years (NAGRA iron container) and between 80,000-400,000 years (KBS copper container). These values are thought to be very conservative. Natural analogues for copper corrosion indicate lifetimes of more than one million years for the KBS container and are probably more appropriate than the archaeological data. Natural analogues for iron corrosion have been inadequately studied, apart from meteorites which are often inappropriate or provide ambiguous data.

3. Chemical data on borosilicate glass waste-form breakdown drawn from studies on volcanic glasses are usually inappropriate. However, these materials provide excellent support for the predictions that:

a) Devitrification will not be a problem on the timescale of interest provided temperatures remain modest.

b) Under the limited flow conditions anticipated in a granite repository the theoretical lifetime of a glass block prior to recrystallisation consequent on hydration could be in the order of 10^7 to 10^8 years provided the surface area/volume ratio is low.

4. Data from the Oklo reactor core zones indicate that the extremely protracted lifetimes (more than 10^8 years) predicted for the dissolution of spent fuel (uranium oxide) waste form are adequately justified for the chemical environment of a granite repository. This is based on observation of the retention of structural, mineralogical and isotopic integrity of the final matrix UO_2 over a timescale of 10^9 years, despite accessibility to groundwater.
In addition the analogue shows the dominance of inter- and intracrystalline diffusion as the release mechanism for fission product elements from the matrix.

5. Elevated temperature fixation of radionculides in wasteform/host rock hydrothermal reaction products is not a significant retardation mechanism if temperatures remain below about 150-200°C. Analogues of chemical retardation based on igneous intrusion or elevated temperature (200-400°C) mineralisation contact zones are inappropriate.
Mineral alteration in the near-field is likely to be dominated by clays (kaolinite, although the buffering effect of the bentonite may lead to smectite formation) whose most useful role will be sorption/permeability control at a later stage rather than direct structural incorporation of radionuclides.

6. The data on groundwater radiolysis and redox conditions in the Oklo core zones is ambiguous in terms of its confirmation or otherwise of the KBS redox model. Concurrent reducing and oxidising reactions seem to have occurred with different effects in terms of bulk mineralogy and radionuclide migration.
The complex nature of the redox conditions in the near-field seems to preclude the simple notion of an oxidation front moving through the rock and mopping up all available reduced species whilst carrying radionuclides with it. Although this concept may be generally conservative, the reality seems to limit radiolytic redox reactions to the very near-field and to allow equal effect to the reducing power of hydrogen as to the role of the oxidants. The localised transport of fission products from the oxidised uraninite (spent-fuel) surface may take place in a reducing fluid with the transport distance controlled more by the kinetics of their re-equilibration to reducing conditions than by the position or even the presence of a distinct redox front.

7. Data from analogues of radionuclide migration during groundwater flow in fractured crystalline rock are only just becoming available, and it has not been possible to provide any quantitative information on the validity of predicted migration rates. However, analogues of natural series (and other) element migration in aquifer systems lends strong support to the validity of transport models although frequently indicating that laboratory retardation factors for individual elements are incorrect. This is clearly one of the main areas where further work is most required.

8. At present natural analogue studies have failed to provide conclusive evidence for the process of matrix diffusion or its likely magnitude in crystalline rocks. The major difficulty is the suitability of samples investigated to date, usually in terms of their chemistry and genesis.

7.2 Conclusions Regarding Future Studies

1. The most important areas where better analogue control is required are in the field of retardation during transport by groundwater flow. Although a few questions and ambiguities remain, and further studies could no doubt offer much greater eventual confidence in our predictions, the requirement for analogues of almost all near-field processes is much less important in terms of the effects on the outcome of a full system performance assessment. This is because such assessments can now generally be shown, on analogue and other evidence, to be extremely conservative in their treatment of these processes.

2. Chapter 6. provided a detailed appraisal of analogue types which could be sought (or where studies were currently getting underway) to enhance our confidence in understanding the major processes involved in release and migration. The most important of these are itemised in brief below:

   a) thermal scale effects in the buffer from studies of contact metamorphism of smectite clays

   b) hydrothermal interaction between waste container metals and the clay buffer (contacts between Cu or Fe rich bodies and smectite rich clays)

   c) more detailed studies of native copper and its environmental behaviour. Initiation of similar work on native iron deposits

   d) use of archaeological material to study specifically the pitting corrosion of iron objects

e) physical studies of fracture frequency, block size and extent of groundwater attack on a fresh volcanic glass body

f) more detailed analysis of inter- and intracrystalline fission product phases in Oklo core uraninite to assess long-term behaviour of spent fuel on possible recrystallisation

g) continued effort on analysis of deep groundwaters from repository environments, uranium ore deposits, and mine tailings to assess radionuclide speciation

h) assessment of mineral fixation and diffusive profiles around low-temperature, late-stage hydrothermal veins in granitic rocks

i) renewed effort to locate natural reactors in uranium ores, with a view to clarifying the nature of radiolysis and redox conditions in the near-field

j) studies of long term stability of magnetite in deep environments from iron ore deposits

k) examination of elemental (particular natural series) mobilities across natural redox fronts and assessment of iron availability in various minerals during oxidation

l) migration studies using a vein containing high natural-series concentrations, transected by a water bearing fissure

m) studies of old (?ancient) metal mine wastes disposed of underground (shafts, pits, etc.) in fractured rocks, and migration in local groundwater regimes

n) analysis of migration away from any geochemical anomalies located in clay sequences or where intersected by major regional fault zones in granite

o) diffusion of chloride into the rock matrix where crystalline rocks have been invaded by sea water.

3. The results of systems assessments (both NAGRA/KBS models and other generic studies) indicates the following ranking of importance of the analogue studies suggested above:

   1. k, l, m, n, o
   2. g, h, i
   3. a, c, d, f, j
   4. b, e

   This ranking reflects not only the relative significance of the processes to which analogues are being applied in affecting the numerical results of systems models, but also the current lack of analogue control on far-field migration processes noted in (1.) above.

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Kurt-Åke Magnusson
Oscar Duran
Swedish Geological Company
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Geochemical simulation of the evolution of granitic rocks and clay minerals submitted to a temperature increase in the vicinity of a repository for spent nuclear fuel

Bertrand Fritz
Marie Kam
Yves Tardy
Université Louis Pasteur de Strasbourg
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Strasbourg, France July 1984

TR 84-11

Smectite alteration

Proceedings of a Workshop Convened at The Shoreham Hotel, Washington, D.C., December 8—9, 1983
Compiled by Duwayne M Anderson
Texas A&M University
November 1984

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Formation of nitric and organic acids by the irradiation of ground water in a spent fuel repository

Hilbert Christensen
Studsvik Energiteknik AB
Nyköping, Sweden 1984-07-13

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The corrosion of zircaloy 2 in anaerobic synthetic cement pore solution

Carolyn Hansson
The Danish Corrosion Centre
Glostrup, Denmark December 1984

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Treatment of zircaloy cladding hulls by isostatic pressing

Ragnar Tegman
Martin Burström
ASEA-CERAMA AB
Robertsfors, Sweden
December 1984

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Sorption of Cs, I and actinides in concrete systems

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