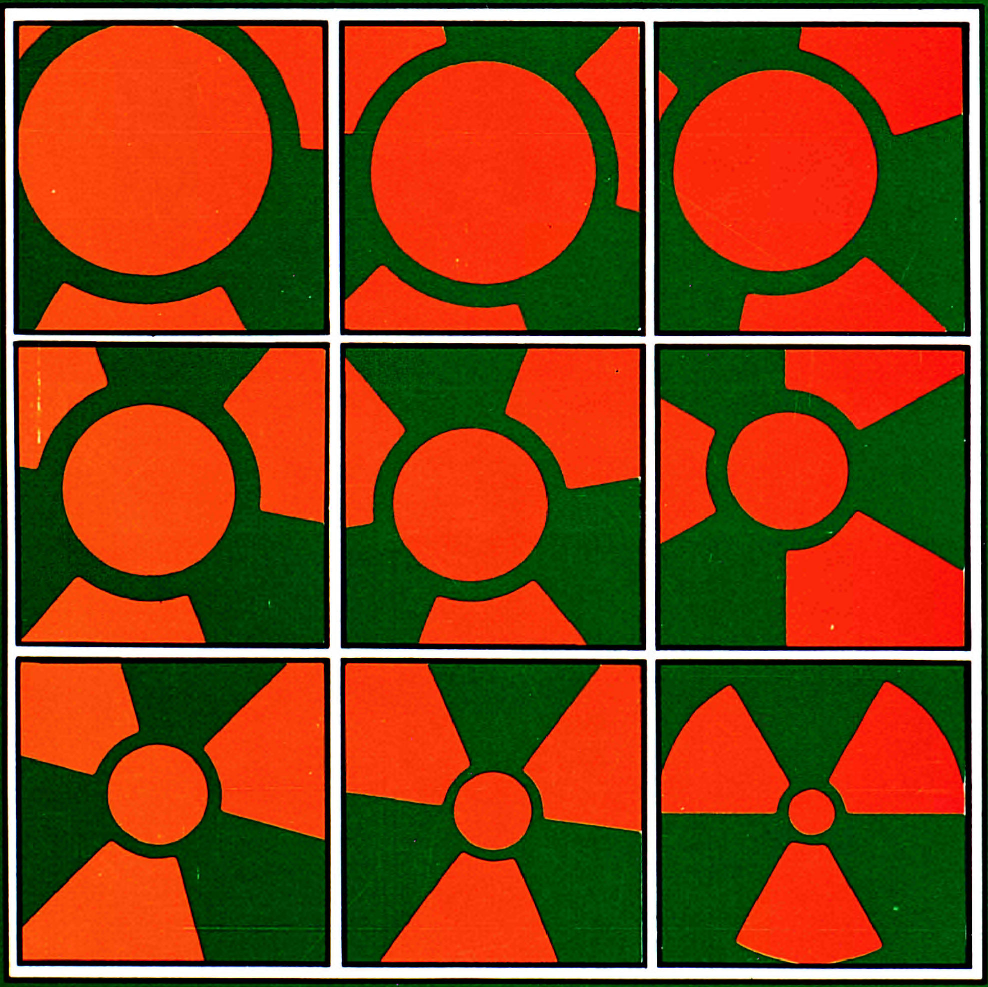
Commission of the European Communities

nuclear science and technology

Fourth natural analogue working group meeting
and
Poços de Caldas project final workshop

Pitlochry, 18 to 22 June 1990, Scotland



Report

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Fourth natural analogue working group meeting and Poços de Caldas project final workshop

Pitlochry, 18 to 22 June 1990, Scotland

Edited by
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Final report

Radiooactive waste management programme

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1990
CEC
NAWG
Poços de Caldas
SCOTLAND

SYNOPSIS

Carefully selected evidences of natural geological systems showing processes analogous to those operating in deep radwaste repositories, called "natural analogues", are now viewed as the most convincing support to long-term performance assessment of geological radwaste disposal. Owing to the considerable upsurge of interest on this topic, and to its own R&D actions in this field, the CEC took the initiative of establishing, in June 1985, a "Natural Analogue Working Group (NAWG)" with a view to offering an international forum for (a) discussion of natural analogue programmes, and (b) assessing their applicability as supports to performance assessments. Since then, the NAWG has held three plenary meetings (1985, 1986, 1988) and a major international symposium (1987).

The fourth meeting of the Group was held in Pitlochry, Scotland, June 18-22, 1990, and also included the final workshop of the Poços de Caldas (Brazil) natural analogue project, sponsored by NAGRA (CH), SKB (S), UK-DOE and US-DOE. About 80 specialists attended this meeting, originating from EC member states, and also Australia, Brazil, Canada, Finland, Japan, Sweden, Switzerland, USA; the IAEA and OECD-NEA were represented by observers. Special thanks are expressed to the British Geological Survey, the hosts and organizers, for the excellent practical arrangements made.

This fourth plenary meeting was the opportunity to review and discuss five years of progress and activities of natural analogues in central areas of performance assessment: waste forms and engineered barriers, geochemistry and radionuclide speciation, radionuclide migration, overall geological context of radwaste disposal. In addition, a "feedback" session provided the opportunity for regulators and those individuals who had advisory roles to give their views and impressions on the significance of natural analogue research.

As results of the meeting, some general observations that summarize the advances made in the five years since the NAWG first met are outlined here:

1. In terms of the technical applications of analogues to performance assessment, they have greatly increased our understanding of relevant processes, and our capability to describe and model them. Five years ago analogue studies tended to be somewhat scorned by purists, but we now have many examples of good, hard testing of models, codes and databases on natural systems. We need more iterations of such testing, particularly "blind" predictive testing, either in relevant environments, or focussed on relevant facets of the models, in order to increase our modelling "muscle".

2. The larger, multi-objective analogue studies (e.g. the Poços de Caldas project) show broad similarities with the process of site investigation for repositories. They are a very cost effective way of training performance assessment groups on real, complex systems. Five years ago such groups had been regarded as passive users of data from analogues; now they are effectively using analogue sites as test-beds.

3. The application of analogues in broadening public perception of the natural context of waste disposal is not yet well developed. Those involved are only just starting to get feedback. There are now significant attempts to use such information in various media for explaining the issues involved in waste and natural radioactivity.

4. We must accept that much of the information stemming from analogue studies is inherently "fuzzy". Where this is the case, it should not necessarily be seen as a drawback, as it simply reflects the complexity of the natural environment. Rather, we should learn from it. If unravelling past events produce fuzzy results, than it is clear that making predictions into the future will give equally, if not more fuzzy results. We are, perhaps, learning to be more realistic about this predictive side of the coin, and appreciating more the unavoidably fuzzy context in which numerical performance assessment results are produced. This will eventually begin to temper the way in which we evaluate and act on these results.

At this occasion, the Core Group* of the NAWG met and discussed possible future activities. It was therefore proposed that a fifth meeting of the NAWG be organized, in 1992, with the objective of reviewing the progress of some major natural analogue programmes, such as Alligator Rivers (ANSTO, Australia, with OECD-NEA sponsorship), Cigar Lake (AECL, Canada) and possibly Oklo (a new phase of work being launched by the French CEA). For this purpose, all necessary aspects will be investigated and announced by the CEC in due course.

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*) Core Group members were, until June 1990: P.L. AIREY (IAEA), N.A. CHAPMAN (INTERA), B. CÔME (CEC), C.J. HARDY (ANSTO), I. McKINLEY (NAGRA), J.C. PETIT (CEA), F.P. SARGENT (AECL), M.E. SHEA (Battelle), J.A. SMELLIE (Conterra).

PROGRAMME OF THE MEETING

Monday 18th June

OPENING SESSION

0930-0940	Welcome (Steven Brown; UKDOE and Per-Eric Ahlström; SKB)
0940-1000	Introduction and Aims (Nicolo Cadelli; CEC)

(Chairman; Nicolo Cadelli)

1000-1030	Making the safety case (Peter Myers; US National Research Council/National Academy of Sciences Board on Radioactive Waste Management).
1030-1100	Coffee
1100-1200	Critical uncertainties in safety assessments and how to address them (Charles McCombie; Nagra)
1200-1330	Lunch

NAWG SESSION 1

The use of information from natural systems in five central areas of performance assessment: Reviews of five years of progress.

1330-1345	Opening of NAWG session. Background and formal matters (Bernard Côme and Neil Chapman).

(Chairmen: Bob Levich and Clarence Hardy)

1345-1445	Review 1: The use of natural analogues in the design and performance assessment of solid radioactive waste-forms (Jean-Claude Petit; CEA)
1445-1545	Review 2: The use of natural analogues in the design and performance assessment of engineered barriers for radioactive waste disposal (Mick Apted; BPNL)
1545-1615	Tea
1615-1715	Review 3: Using hydrogeochemical data from natural environments to improve models of radionuclide speciation in groundwaters (David Read; Atkins, and Paul Hooker; BGS)

Tuesday 19th June

(Chairmen: Y. Yusa and David Billington)

0900-1000	**Review 4:** Using data from natural environments to improve models of radionuclide migration in groundwaters (Russell Alexander; University of Bern)
1000-1100	**Review 5:** Putting performance assessment results in a broader geological context (Peter Sargent; AECL)
1100-1130	**Coffee**

POÇOS DE CALDAS PROJECT WORKSHOP

(Chairmen: Per Eric Ahlström and Mike Ferrigan)

1130-1135	Introduction (Neil Chapman; Intera-ECL)
1135-1205	Previous studies in the area (Eduardo Penna Franca; Federal University of Rio de Janeiro)
1205-1230	Project History and Overview of the Sites (John Smellie; Conterra)
1230-1400	**Lunch**
1400-1500	A Performance Assessment Guide to the Project (The Project Technical Committee)

Presentation of detailed papers by principal investigators

1500-1530	Geomorphology and hydrogeology (David Holmes; BGS)
1530-1600	**Tea**
1600-1640	Mineralogy and petrology of the Osamu Utsumi mine (Hans Schorscher; University of São Paulo)
1640-1700	Trace element distribution across the redox front (Gus Mackenzie: SURRC)
1700-1730	Mineralogy and petrology of Morro do Ferro (Niklaus Waber; University of Bern)
1730-1800	Hydrogeochemistry (Kirk Nordstrom: USGS)
After Dinner	NAWG Core Group Meeting

Wednesday 20th June

POÇOS DE CALDAS PROJECT
Presentation of detailed papers by principal investigators (continued)

(Chairmen: Fred Karlsson and Nick Harrison)

0900-0930	Geological evolution of the Poços de Caldas plateau (Tjerk Peters; University of Bern)
0930-0945	Microbiology (Julia West; BGS)
0945-1005	Rare-earth and radiochemistry of groundwaters (Paul Linsalata; University of New York)
1005-1035	Colloids and particulates in groundwaters (Norbert Miekeley: PUC)
1035-1105	Trace element hydrochemical modelling (Jordi Bruno; KTH)
1105-1130	Coffee
1130-1150	Radiochemistry of the rocks (Gus Mackenzie; SURRC)
1150-1210	Redox front radiochemical modelling (Roger Scott; SURRC)
1210-1240	Redox front mineralogical modelling (Peter Lichtner; Bern)
1240-1400	LUNCH
1400-1430	Redox front migration (Ivars Neretnieks; KTH)
1430-1500	Hydrothermal transport modelling (Larry Cathles: Cornell)
1500-1630	**Summary: Implications for Performance Assessment** A structured discussion led by the Technical Committee
1730	High Tea

Thursday 21st June

NAWG SESSION 2: Workshop Sessions
Discussion and development of issues arising from the introductory review lectures

0915-0930	Introduction (Neil Chapman and Bernard Côme; who will also act as rapporteurs for each session, assisted by the co-chairmen)
0930-1030	Workshop Session 1: Waste-form and engineered barrier behaviour *(Chairman; Tönis Papp; Co-chairman; Jean-Claude Petit)*
1030-1100	Coffee
1100-1200	Workshop Session 2: Geochemistry and speciation of radionuclides in groundwaters *(Chairman; Mick Apted; Co-chairman; David Read)*
1200-1330	Lunch
1330-1430	Workshop Session 3: Radionuclide migration and sorption *(Chairman; Jordi Bruno: Co-chairman; Russell Alexander)*
1430-1530	Workshop Session 4: Using data from natural systems to put assessment results into context *(Chairman; Ferruccio Gera; Co-chairman; Peter Sargent)*
1530-1600	Tea
1600-1700	Formal Poster Session
1700-1800	Poços de Caldas Project Steering Group Meeting

Friday 22nd June

Feedback Session
Natural Systems, and the interpretation of assessment results in the context of regulatory requirements and public perception

0930-1100 Organised as a PANEL SESSION with the following panelists:

Chairman: Steve Brown (HMIP, UK Dept. Environment)

Panelists: Ken Bragg (AECB, Canada)
George Hornberger (USNAS Board on Rad. Waste Management)
Pierre Escalier des Orres (CEA, France)
Ueli Niederer (HSK, Switzerland)

1100-1130	**Coffee**
1130-1145	**Summary:** Nicolo Cadelli; Bernard Côme (CEC)
1145-1200	Close: Announcements on reporting and publications, future of NAWG programme, initiatives arising from meeting, etc. (Bernard Côme and Neil Chapman)
1200-1330	**Lunch**
1400	Transport departs for Edinburgh (Airport and Railway Station)

INTRODUCTION AND AIMS

by N. CADELLI, CEC

On behalf of the Commission of the European Communities, which sponsored and coordinated the activity of the Natural Analogue Working Group, I have the pleasure to welcome all the participants to this special meeting, the 4th of the series since the group met for the first time in 1985.

As far as I know, this meeting is the only international event entirely devoted to the theme of natural analogues during this year.

As a matter of fact, the necessity of reviewing the outputs of major national and international actions in the field of radwaste disposal was felt - probably not by pure coincidence - by a number of organisations at about the same time. I would like to mention some recent examples :

* the CEC-NEA-IAEA sponsored symposium on the safety of the geological disposal, Paris, October 1989

* and, more recently, the GEOVAL 90 symposium, organised by SKI with the sponsorship of OECD-NEA.

During all these meetings, the necessary comparison of our safety calculations with some convincing experimental data from natural systems was an underlying - although not major - theme of discussion. Therefore, our own fourth NAWG meeting appears to be particularly topical and welcome.

I would like to underline the opportunity we had to include in the agenda the Poços de Caldas workshop ; this is an example of the excellent cooperative spirit with which the NAWG is viewed by all the participants and by the various organisations involved in our activities. I would like to thank all the sponsors of the Poços de Caldas projects, with most of which the CEC has a cooperation agreement, and in particular SKB, who ensured the organisation of this part of our agenda, which is the final review of the three-year project now ended.

I spoke about a special meeting and, indeed, it is intended to follow a somewhat different scheme as our previous meetings. It appeared that after five years of activity, time has come to review the progress accomplished in the natural analogue activities and to assess the achievements.

The work on natural analogues is not meant as an isolated activity in the field of waste disposal, but it has been recognised by the NAWG during the previous meeting at Snowbird (1988), for example, as an essential component in performance assessment studies.

Having conducted the PAGIS and PACOMA exercises, I am particularly aware of the weak points of present performance assessments, where the natural analogues can be the only available support for predicting the repository behaviour in the short, the medium and in the long term.

The areas for support cover the identification of phenomena, the validation of models, the "feeling" about the behaviour of the various barriers, and in particular, the far-field. This last point is of paramount importance in another context : the complexity of performance assessment studies are seen with suspicion and mistrust by the general public, what can be understood, in particular where predictions are made over millions of years. But millions of years are the geological times over which are being developed the events and phenomena making the object of natural analogue studies. Their analyses and results can be worked out as acceptable examples of the rock capabilities of segregating various materials, or identify the conditions for enhanced particle movements during very long time periods.

All these points and others were stated already during the last meeting of the group. The objective of the present NAWG are intended to be more specific and practical and to draw up the basis for the future activity in the field.

In order to achieve these objectives, the meeting will start with two papers introducing the "safety case" and outlining the major difficulties in performance assessments and in particular the question of uncertainties.

Five review papers on five specific topics will then be presented. They will not only be progress reports, but I hope that the practical support to safety assessments will be examplified and, also with the help of the discussions, the way and the extent of the interaction between natural analogues and Performance Assessment will be indicated, for instance, in the field of model validation. There are problems here, which are not yet clarified, since on one hand the level of an acceptable validation has not been defined and, on the other hand, even very simple models appear to require site specific validation insofar as the basic phenomena have not all been given a proven theoretical background.

The Poços de Caldas Workshop inscribes perfectly in the following session, since it is going to review four facets of the work, thus complementing the previous sessions. It will be followed by a series of detailed papers on the various study areas of the Project.

I hope that we will succeed in explicitating the achievements for all what concerns the understanding of the simple phenomena involved, the support to performance assessment models and the way natural analogues may provide global, understandable evidence of the retention/retardation capability of the natural and man-made barriers, in order to put performance assessment results into perspective. This is, indeed, the objective of the Thursday session, one of the most important parts of our meeting, which shall try to draw the practical conclusions from the presentations and discussions of the first two days.

The last day is devoted to a theme, which is no more simply a technical matter, since this panel session will tackle a particularly important matter including the regulatory requirements and the public perception. I hope, that the NAWG will be able to transmit in practical terms a clear message on the use of natural analogues in that context.

The CEC is highly interested in the outcome of this meeting, especially of the last two sessions, since, as you probably know, we are in the process of selecting the shared-cost actions of our 4th five-year programme on Radioactive Waste Management & Disposal, launched this year.

On one side we are going to continue the technical work already started years ago and to readapt it to the present requirements and level of knowledge; on the other side, an essential effort of the CEC programme will be devoted to activities of pre-normative character, as foreseen in the CEC Plan of Action. In this context, may I mention the report EUR 12570 "Objectives, standards and criteria for radioactive waste disposal in the E.C", the first one to be published in the new EURADWASTE series.

I would not like to close this introduction without recalling that in September 1990, during the week of 17-21, the Third Community Conference will take place in Luxembourg, where the activities and the results of the third CEC programme on Radioactive Waste Management & Disposal will be presented. You are all invited to attend.

With this final word, I wish you a successful meeting in Pitlochry.

NAWG INVITED PAPERS

RETHINKING HIGH-LEVEL RADIOACTIVE WASTE DISPOSAL: MAKING THE SAFETY CASE

F.L. PARKER
Vanderbilt University, USA

(Presented for F.L. Parker by P.B. Myers, National Research Council)

Summary

There is worldwide consensus that geological disposal is best for disposing of high-level radioactive waste; nevertheless, the U.S. program is unlikely to succeed. The program is hampered by its high degree of inflexibility with respect to both schedule and technical specifications that assume the properties and future behavior of a geological repository can be determined and specified with a very high degree of certainty.

Geological models, and scientific knowledge generally, have been inappropriately applied. Geophysical analysis can and should have a key role in the assessment of long-term repository isolation; however, geophysical models are being asked to predict the detailed structure and behavior of sites over thousands of years. This is scientifically unsound and will lead to bad engineering practice.

The United States has written detailed regulations for repository siting and construction before all of the data are in and is thus bound by requirements that may be impossible to meet. An alternative approach emphasizing flexibility can succeed. It will require time to assess performance, a willingness to respond to problems as they arise, remediation if necessary, and revision of the design and regulations if they are found to impede progress toward the health goal already defined as safe disposal.

This presentation is a digest of a position paper "Rethinking High-Level Radioactive Waste (HLW) Disposal"[1] prepared by the Board on Radioactive Waste Management (BRWM or Board) of the National Research Council. The National Research Council is the operating arm of the National Academies of Science and Engineering and the Institute of Medicine.

The conclusions in this paper are the result of several years of the Board's discussions and, therefore, have a strong base in the decades of scientific and professional experience represented among its members. This experience was augmented at a week-long study session in Santa Barbara, California in July 1988 to which the Board invited experts from the United States and abroad.

This group identified two reasons why the technical programs on high level radioactive waste disposal carried out by government and industry in the United States have not led to a socially satisfactory resolution of the problem of High-Level Waste (HLW) management and disposal. The first and most obvious is the controversy over nuclear energy and radioactive waste disposal as part of nuclear energy development. The Board takes no position on the use of nuclear energy. But, it notes that even if nuclear power were discontinued tomorrow--a highly unlikely event--we would still need to dispose of nuclear waste from existing power plants and defense programs, and we would, therefore, still require a viable HLW disposal program. The second reason that radioactive waste management remains in trouble is the way in which the programs have been designed and carried out. The Board believes that important scientific and technical issues concerning HLW have been widely misunderstood; the result is a set of programs that will not achieve their stated goals. Neither the technical nor the social problems of the waste materials already in existence are being handled effectively. Still, the Board believes that the safe and effective isolation of radioactive waste is feasible.

At our study session, the group divided its deliberations among four topics: (1) the limitations of analysis or what can we really know?; (2) modeling and its validity; (3) moral and value issues; and (4) strategic planning. These categories also determine the structure of this paper, although in the analysis here, as in the real world, there is no easy separation among them.

Although this paper is critical of present policies, it must be emphasized that the changes that need to be made are not restricted to the U.S. government. The nature of the risks and the government's responsibility to address them need to be presented and understood in terms different from those reflected in public policy. Doing so will not lead to less safety but to more. Yet, achieving that result will require courage on the part of leaders in government and industry, as well as a willingness to rethink risks among the public at large and in the interest groups concerned with public policies for the management of risk.

Current U.S. Policy and Program

In the Nuclear Waste Policy Act of 1982 (NWPA)[2] Congress assigned responsibility to the Department of Energy (DOE) for designing and eventually operating a deep geological repository for high-level radioactive waste. The repository must be licensed by the U.S. Nuclear Regulatory Commission (NRC) and must meet performance standards established by the U.S. Environmental Protection Agency (EPA) and regulations issued by the NRC.

The U.S. program is unique among those of all nations in its rigid schedule, in its insistence on defining in advance the technical requirements for every part of the multibarrier system, and in its major emphasis on the geological component of the barrier. Because nuclear waste management necessitates predicting the fate of HLW into the distant future, the undertaking is necessarily full of uncertainty. And accounting for uncertainty runs counter to DOE's mode of operation.

For historical and institutional reasons, DOE managers seem to feel compelled to do things perfectly the first time, rather than to make changes in concept and design as unexpected geological features are encountered and as scientific understanding develops. This "perfect knowledge" approach is unrealistic, given the inherent uncertainties of this unprecedented undertaking, and it runs the risk of encountering "show-stopping" problems and delays that could lead to a further deterioration of public and scientific trust. In this sense the government's HLW program and its regulation may be a "scientific trap" for DOE and the U.S. public alike, encouraging the public to expect absolute certainty about the safety of the repository for 10,000 years and encouraging DOE program managers to pretend that they can provide it. To date, because of the regulatory requirements and the way the program is being carried out, U.S. policy has not led to satisfactory progress on the problem of radioactive waste disposal.

There is a strong worldwide consensus that the best and safest long-term option for dealing with HLW is geological isolation. High-level waste should be put into specially designed and engineered facilities underground, where the local geology and groundwater conditions have been chosen to ensure isolation of the waste for tens of thousands of years or longer, and where waste materials will migrate very slowly if they come into contact with the groundwater.

Although the scientific community has high confidence that the general strategy of geological isolation is the best one to pursue, the challenges are formidable. In essence, geological isolation amounts to building a mine in which the "ore" will be put back into the ground rather than taken out. Mining, however, has been and remains fundamentally an exploratory activity: because our ability to predict rock conditions in advance is limited, miners often encounter surprises. Over the years, mining engineers have developed methods to deal with the vagaries of geological environments, so that mineral extraction and construction can continue safely even when the conditions encountered are different from those anticipated.

It is at this point that geological isolation of radioactive waste differs in an important sense from mining. In the United States, radioactive waste management is a tightly regulated activity, surrounded by laws and regulations, criteria and standards. Some of these rules call for detailed predictions of the behavior of the rock for the tens of thousands of years that the radioactive materials are to be isolated.

Preparing quantitative predictions so far into the future stretches to the limit our understanding of geology, groundwater chemistry and movement, and their interactions with the emplaced material (radioactive waste package, backfill, sealants, and so forth). Although the basic scientific principles are well known, quantitative estimates (no matter how they are obtained) must rely on many assumptions. As a consequence, the resulting estimates are uncertain to some degree, and they will remain uncertain no matter how much additional information is gathered.

The character and implications of these uncertainties must be clearly understood by political leaders, program managers, and the concerned public. Engineers and scientists, no matter how experienced or well trained, are unable to anticipate all of the potential problems that might arise in trying to site, build, and operate a repository. Nor can science "prove" (in any absolute sense) that a repository will be "safe" as defined by EPA standards and NRC regulations. This is so for two reasons.

First, proof in the conventional sense cannot be available until we have experience with the behavior of an engineered repository system--precisely what we are trying to predict ahead of time. The existence of uncertainties has prompted efforts to improve the technical analysis, but there will always remain some residual uncertainty. It is important to recognize, however, that uncertainty does not necessarily mean that the risks are significant. What it does mean is that a range of results are possible, and a successful management plan must accommodate residual uncertainties and still provide reasonable assurance of safety.

Second, safety is in part a social judgment, not just a technical one. How safe is safe enough? Is it safer to leave the waste where it is, mostly at reactor sites, or to put it in an underground repository? In either case safety cannot be 100 percent guaranteed. Technical analyses can provide background for answering such questions, but ultimately the answers depend on choices made by the citizens of a democratic society. The EPA has not based its standards on such realistic alternatives. Both of these important limitations of the analysis (no proof in the conventional sense and safety as a societal decision), have been understated.

To secure the public trust, the federal government must provide full accountability as information about the risks changes with experience. This is not an impossible task: government and business make decisions every day under similar conditions of uncertainty. But a policy that promises to anticipate every conceivable problem, or assumes that science will shortly provide all the answers, is bound to fail.

The public has been told too often that absolute guarantees can be provided, but most citizens watching the human frailties of their governments and technologists know better. A realistic--and attainable--goal is to assure the public that the likelihood of serious unforeseen events (serious enough to cause catastrophic failure in the long term) is minimal, and that the consequences of such events will be limited. These assurances rest on the credible application of general principles, rather than a reliance on detailed predictions.

The Limitations Of Modeling For Geological Processes

The current U.S. approach to developing a geological repository (with a mandated 10,000-year lifetime) for radioactive waste is based on a regulatory philosophy that was developed from the licensing of nuclear power plants (which have a nominal 40-year lifetime). The geological medium, however, cannot be specified in advance to the degree possible for man-made components, such as valves or electronic instruments, nor can it be tested over its projected lifetime as can many man-made components. Commercial mining and underground construction both operate on the sound principle of "design (and improve the design) as you go." The inherent variability of the geological environment necessitates changes in specifications as experience increases. If that reality is not acknowledged, there will be unforeseen delays, rising costs, frustration among field personnel, and loss of public confidence in the site and in the program.

Models of the repository system are useful, indeed indispensable. The computerized mathematical models that describe the geological structure and hydrological behavior of the rock are needed to manage the complex calculations that are necessary to evaluate a proposed site. Models are vital for two purposes: (1) to understand the history and present characteristics of the site; and (2) to predict its possible future behavior. Putting the available data into a coherent conceptual framework should focus attention on the kinds of uncertainty that exist.

For example, the modeling of groundwater flow through fractured rock lies at the heart of understanding whether and how a repository in hard rock will perform its essential task of isolating radioactive materials. The studies done over the past two decades have led to the realization that the phenomena are somewhat more complicated than had been thought. Ground water modelling is better understood than almost any other component of the repository system, yet as Leonard Konikow points out in a post audit of the accuracy of ground water models, the results are not totally satisfactory.[3] Rather than decreasing our uncertainty, this line of research has increased the number of ways in which we know that we are uncertain. This does not mean that science has failed; we have learned a great deal about these phenomena. But it is a commonplace of human experience that increased knowledge can lead to greater humility about one's ability to fully understand the phenomena involved.

Uncertainty is treated inappropriately in the simulation models used to describe the characteristics of the waste repository. As the quantity of information about natural geological settings grows, so too does our appreciation of their variability and unpredictability. This point has often been ignored. Indeed, the very existence of large databases and sophisticated computer models suggests, erroneously, that it is appropriate to design a geological repository as if it were a nuclear power plant or jet airliner, both of which have predictable attributes over their relatively short lifetimes. That assumption of accurate predictability will continue to produce frustration and failure.

Under the present program, models are being asked to provide answers to questions that they were not designed to address. One scientifically sound objective of geological modeling is to learn, over time, how to achieve reasonable assurance about the long-term isolation of radioactive waste. That objective is profoundly different from predicting quantitatively the long-term behavior of a repository. Yet, in the face of public concerns about the safety of HLW disposal, DOE has done exactly that!

The Board believes that this use of geological information and analytical tools--to pretend to be able to make very accurate predictions of long-term site behavior--is scientifically unsound. Its conclusion is based on detailed reviews of the methods used by DOE and the regulatory agencies in implementing the Nuclear Waste Policy Act.[2]

Well-known geophysical principles can be used to estimate or to set bounds on the behavior of a site, so that its likely suitability as a waste repository can be evaluated. But it is inappropriate to stretch the still incomplete understanding of a site into a quantitative projection of whether a repository will be safe if constructed and operated there. Only after a detailed, lengthy, and costly examination of the site itself can an informed judgment be reached, and even then, there will still be uncertainties.

Many of the uncertainties associated with a candidate repository site will be technically interesting but irrelevant to overall repository performance. Further, the issues that are analytically tractable are not necessarily the most important. The key task for performance modeling is to separate the significant uncertainties and risks from the trivial. Similarly, when there are technical disputes over characteristics and processes that affect calculations of waste transport, sensitivity analysis with alternative models and parameters can indicate where further analysis and data are required and where enough is known to move on to other concerns.

It may even turn out to be appropriate to delay permanent closure of a waste repository until adequate assurances concerning its long-term behavior can be obtained through continued in-situ geological studies. Judgments of whether enough is known to proceed with placement of waste in a repository will be needed throughout the life of the project. But these judgments should be based on a comparison of available alternatives, rather than a simplistic debate over whether, given current uncertainties, a repository site is "safe." Even while the detailed, long-term behavior of an underground repository is still being studied, it may be marginally safer to go ahead and store reactor waste there (in a way that permits retrieval if necessary), rather than leaving it at reactors.

As a rule, the values determined from models should only be used for comparative purposes. Confidence in the disposal techniques must come from a combination of remoteness, engineering design, mathematical modeling, performance assessment, natural analogues (see below), and the possibility of remedial action in the event of unforeseen events. There may be political pressure on implementing agencies to provide absolute guarantees, but a more realistic--and attainable--goal is to assure the public that the likelihood of unforeseen events is minimal, and that the magnitude of the consequences of such events is limited. Such an alternative approach, now being used in Canada and Sweden, promises to be far more successful in achieving a safe and practical waste disposal system.

Moral and Ethical Issues

Radioactive waste certainly poses hazards that raise moral and ethical concerns. First, some of the radioactivity lasts for extremely long periods of time--the EPA standard for HLW calls for isolation of the waste for 10,000 years and more, a time longer than recorded human history. Second, the risks of HLW will be concentrated at a very few geological repositories. The neighbors of proposed waste repositories have understandably been alarmed at the prospect of hosting large quantities of a material that needs to be handled with great care. Ethical studies in this area underscore two points: (1) the central role of a fair process; and (2) the pervasive problem of promising more certainty than can be delivered.

The need for a fair process is simply stated: people feel threatened by radioactive waste; and they deserve to be taken seriously in the decision-making process. The sense of threat is often ill informed, in a narrow technical sense; but when it occurs, it is the duty of technical experts and program managers to provide information and to employ analyses that will be credible to the affected populations. Only with information that they believe can those affected parties participate and negotiate equitable solutions. The primary goal of the program is to provide safe disposal; a secondary goal is to provide it without any gross unfairness. As a result, the mechanisms of negotiation, persuasion, and compensation are fundamental parts of any program to manage and dispose of radioactive waste--not mere procedural hoops through which program managers must jump.

The second ethical point is also important: the demand for accountability in our political system has fostered a tendency to promise a degree of certainty that cannot be realized. Pursuing that illusory certainty drives up costs without delivering the results promised or comparable benefits. The consequence is frustration and mistrust. For example, it is politically costly to admit that one has been surprised in exploring sites being considered for HLW repositories. Yet, this situation is self-defeating; surprises are bound to occur because a principal reason for exploration is to discover what is there.

In looking at equity, there are three issues, each of which raises concerns of differential impact, public values, and moral accountability.[4] (1) Who does the work and who pays for it? (2) What do we owe to future generations? (3) Who benefits and who is exposed to risk?

These ethical concerns are investigated in a recent study in relationship to five key policy issues in waste disposal.[5] The study discusses the "fairness" and appropriateness of the procedures for making decisions, the distribution of costs and benefits, and the type of evidence that is considered sufficient and admissible. The study places special emphasis on the role of scientific evidence because of the large scientific uncertainties and the continuing controversy, even among experts, on what is known and not known.

The first issue is the need for the repository. The core policy dispute concerns the choice between immediate permanent disposal in a geologic repository and indefinite long-term monitored storage in an engineered facility (including at-reactor storage) at or near the surface. The controversy has been over the distribution of costs and benefits to current and future generations and to various stakeholder groups. All stakeholder groups agree that this generation should fulfill its responsibility to future generations but they disagree on how to turn this valuable principle into policy.

The second issue is siting. In making politically difficult siting decisions, political leaders have two basic options: make the choice internally and impose it on a weak constituency; or set up and follow a selection process perceived across the board as objective, scientifically credible, and procedurally fair.

The third issue is intergovernmental sharing of power. Procedural values were also important in NWPA, which established rules for sharing power among the affected governmental entities. Today the State of Nevada interprets the 1987 NWPA Amendments as unfair on procedural as well as distributional and evidential grounds.

The fourth issue is safety. The fundamental safety issue is the determination of a fair evidential process and standard of proof for showing that the repository is acceptably safe for the thousands of years over which the waste will remain dangerously radioactive. The evidential uncertainties in assessing repository safety may point to a more flexible and evolutionary approach, but this conflicts with DOE's concern with keeping to a fixed schedule, so as to limit costs, discharge obligations to future generations, and meet contractual commitments to utilities holding spent fuel.

The final issue concerns impacts. The debate over the distributional impacts of the repository program include such issues as who should pay for the cost of the program, how the impacts can be fairly calculated, and what is fair compensation for negative impacts.

Consideration of these policy debates regarding the disposal of radioactive waste leads to three important conclusions:

- no interested party has an exclusive claim to be rational or to articulate the public interest;
- what is considered fair or unfair is subjective and can change over time; and
- with regard to repository safety, the issue is acceptability rather than certainty. Acceptability is what is acceptable to society, given the evidential uncertainties, perceptions of risk, and contentious stakeholder debates.

These conclusions highlight the advantage of an empirical approach--one that examines fairness in process, outcomes, and evidence; one that reflects an understanding of the values as well as the interests of the stakeholders. Such an approach may lead to policies that have a greater chance of surviving over time because they are more widely perceived as fair.

Instead of pursuing an ever-receding mirage, it is sensible to pursue an empirical exploratory approach: one that emphasizes fairness in the process while seeking outcomes that the affected populations judge to be equitable in light of their own values. This will not be an easy course, but it is necessary.

Strategic Planning

As we have noted earlier, there is no scientific reason to think that an acceptable HLW repository cannot be built and licensed, but for historic and institutional reasons, DOE managers often feel compelled to "get it right the first time" and this management strategy runs the risk of encountering "show-stopping" problems that may delay licensing and will certainly cause further deterioration of public and scientific trust.

An alternative management strategy would be more flexible and experimental, and would embody three principles:

- respond with conservative design changes as site attributes are discovered;
- use modeling to identify areas where more information is needed; and
- allow for remediation if things do not turn out as planned.

Implicit in this approach is the need to revise both technical design <u>and regulatory criteria</u> as more information is discovered. This is difficult to achieve in a governmental structure that disperses authority among legislative and executive agencies, and also separates regulation from implementation. When presented with intense controversy, such an institutional arrangement breeds distrust both among governmental units and widely in the public. In that setting, partial remedies further entangle the procedural morass.

As the current U.S. program seems unlikely to succeed, the Board proposes an alternative approach that is built on well-defined goals and objectives, utilizes established scientific principles, and can be achieved with known management capabilities. What is needed is an institutional approach that is more flexible and experimental--in other words, a strategy that acknowledges two important premises:

- * Surprises are inevitable in the course of investigating any proposed site, and things are bound to go wrong on a minor scale in the development of a repository.
- * If the repository design can be changed in response to new information, minor problems can be fixed without affecting safety, and major problems, if any appear, can be remedied before damage is done to the environment or to public health. This flexible approach can be summarized in three principles:
- ** Start with the simplest description of what is known, so that the largest and most significant uncertainties can be identified early in the program and given priority attention.
- ** Meet problems as they emerge, instead of trying to anticipate in advance all the complexities of a natural geological environment.
- ** Define the goal broadly in ultimate performance terms, rather than immediate requirements, so that increased knowledge can be incorporated in the design at a specific site.

In short, this alternative uses a scientific approach, and makes use of modeling to identify areas where more information is needed, rather than to justify decisions that have already been made on the basis of limited knowledge.

The principal virtue of this strategy is that it would use science in a deductive, rather than a speculative, way--as science should be used. It would be similar to the strategies now being followed in Canada and Sweden, where the exploration and construction of an underground test laboratory and a shallow underground low-level waste repository have followed a flexible path. At each step, information and understanding developed during the prior stages are combined with experience from other underground construction projects, in order to modify designs and procedures in light of the growing stock of knowledge. During operation and after closure of the facilities, emphasis will be placed on monitoring and assuring the capability to remedy unforeseen problems. In that way, the possibility is minimized that unplanned or unexpected events will compromise the integrity of the facility.

This flexible approach has more in common with research and with underground exploration than with conventional engineering practice. The idea is to draw on natural analogues, integrate new data into the expert judgments of geologists and engineers, and take advantage of favorable surprises or compensate for unfavorable ones.

Natural analogues--geological settings in which naturally occurring radioactive materials have been subjected to environmental forces for millions of years--demonstrate the action of transport processes like those that will affect the release of man-made radionuclides from a repository in a similar setting. Where there is scientific agreement that the analogy applies, this approach provides a check on performance assessment methodology and may be more meaningful than sophisticated numerical predictions to the lay public.

An essential element of this broader scientific approach is the use of the professional judgment of technical experts as an input to modeling in areas where there is uncertainty as to parameters, geologic structures, or even future events. Such judgments, which may differ from those of DOE program managers, should be incorporated early in the process; a model created in this way might redirect the DOE program substantially.

The large number of underground construction projects that have been completed successfully around the world are evidence that this approach works well. Implicit in this approach, however, is the need to revise the program schedule, the repository design, and the performance criteria as more information is obtained. Unfortunately, in the United States, putting such an approach into effect would require major changes in the way Congress, the regulatory agencies, and DOE conduct their business.

The Risk Of Failing To Act

Given the history of radioactive waste management in the United States, it is likely that the program will continue as at present. That would leave the nation's inventory of high-level waste, indefinitely, where it is now: mostly at reactor sites on or near the earth's surface. This alternative is safe in the short term--onsite storage systems are safe for at least 100 years, according to present evidence.[6] But at-surface storage by default may be irresponsible for the long run because of the uncertainties associated with maintaining safe institutional control over HLW at or near the surface for centuries.

In judging disposal options, therefore, it is essential to bear in mind that the comparison is not so much between an ideal system and imperfect reality as it is between a geologic repository and at-surface storage. From that standpoint, both technical experts and the general public should be reassured by a conservative engineering approach toward long-term safety, combined with an institutional structure designed to permit flexibility and remediation.

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BIBLIOTHEQUE

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CRITICAL UNCERTAINTIES IN SAFETY ASSESSMENTS AND HOW TO ADDRESS THEM

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SUMMARY

Safety assessment is a very wide field which includes developing an understanding of a disposal system, quantifying the behaviour of this system, assessing the limitations of such predictions and, very importantly, convincing relevant groups of the adequacy of the overall analysis. This paper discusses the uncertainties invovled in each of these areas and considers the roôle which is, or could be, played by natural analogues.

INTRODUCTION

The aim of this talk, according to the programme committee which chose the topic is to "put the current meeting into context". This explicit acknowledgement that we in the waste management community are studying natural analogues within the specific context of assessing the safety of radioactive waste disposal is a healthy reminder of the practical, project-oriented basis of our work. In fact, since the rapid increase in analogue studies during the early 1980s, there has always been a strong emphasis on their relevance to analyses of repository behaviour. All of the major meetings on analogues have directed attention to the rôles of natural analogues in providing data, helping our understanding of processes and increasing our confidence in our predictive abilities.

As a result, a valuable series of overviews have been presented by highly competent authors [Refs. 1-5]. In preparation for the current talk, I looked through these earlier papers produced under the auspices of the CEC Natural Analogue Working Group (NAWG) and concluded - to my apprehension - that little appeared to be left to say! The most recent NAWG meeting in 1988 led to a written summary of "the issue of how natural analogues can be used in support of performance assessments, both in justification of the results and presentation to the public". In my contribution to this Symposium I shall not re-iterate all of the good advice to date. Instead I shall try

- to take into account newer opinions on the status of safety assessments (as expressed, for example, at recent international symposia)
- to comment specifically upon the often-mentioned, but seldom fully utilised, rôle of natural analogues in enhancing confidence of "non-experts" (i.e. decision-makers and public).

Before becoming specific, however, I would first like to make sure that we all have a common understanding of the important concepts in the title, namely "safety assessment" and "critical uncertainties".

It may seem trivial to ask what we all understand by safety assessment or analysis - after all dozens of meetings have been held on the topic and hundreds of reports and papers produced. Recently, however, I have noticed some divergence of views coming to light - for example in discussions at the NEA/IAEA/CEC Symposium on Safety Assessment in Paris 1989, in the following debate within the organizations mentioned on a proposed "common opinion" on the status safety assessment, and in discussions at the GEOVAL 1990 Symposium on Validation of Geosphere Models. Safety assessment, in my opinion and that of most practitioners of the discipline, is not just a calculational framework for cranking out numerical predictions of system behaviour. This narrow view has led to unjustified criticism of modelling efforts by some groups outside the field and equally unjustified overemphasis on development of unnecessarily complex computer models by others in the field.

Safety analysis is to be understood as a broad activity aimed at the following major goals:

- Developing a sufficient understanding of the physical and chemical behaviour of a disposal system
- Quantifying this understanding in order to allow predictions of future system behaviour
- Assessing the possible errors in our predictions and the likelihood of these errors occurring
- Convincing all relevant groups (project staff, regulators, public) of the adequacy of the analyses.

In our technical jargon, these points are covered in the development of, respectively, conceptual models, computational models, uncertainty analyses and validation techniques. In all areas data are needed. Experimental results produced in the laboratory or in the field are complemented by observations in the field and by investigation of natural analogues, the subject of this meeting.

In discussions the "safety assessment" of our title we take, then, a wide view. What do we mean by "critical uncertainties"? These clearly affect the goals of safety assessment listed above. In a more general sense, however, critical uncertainties are those which affect our decision-basis for planning, analysing and implementing repositories. They are not necessarily the numerically largest uncertainties in the analyses. Obviously critical uncertainties may be perceived differently by different groups. The groups at this meeting (according to the original information sheet) are "those involved in:

- research into natural analogues and natural geological migration systems
- carrying out or interpreting performance assessments of radioactive waste disposal
- giving guidance to government departments on waste disposal issues
- enhancing public awareness of the safety aspects of radioactive waste disposal."

Clearly, these may all perceive differing critical uncertainties, dictated by their programme involvement (and their personal interests).

The most straightforward group, at least in some specific circumstances, is that of the performance assessors. These can often use structured techniques to quantify uncertainties and can objectively rank them in order of importance by measuring against given performance targets. Accordingly, much effort has been recently invested in this area and correspondingly large advances achieved. The communication problem with other groups, however, can also be well illustrated here. An outside observer at the 1989 Safety Symposium in Paris concluded directly from the many technical discussions on uncertainty analysis that the waste management community is highly unsure of what it is doing! I shall mention the tractable problem of quantifying particular types of uncertainty again later, but I shall also try to look at uncertainties perceived by other groups.

Let us move now to a discussion of critical uncertainties within the 4 main components of safety assessment as mentioned above.

UNDERSTANDING SYSTEM BEHAVIOUR

In this first, most important step, it is conventional to separate out a scenario question (what future system states may occur with what probabilities?) and a more detailed process part (do we understand all relevant physical and chemical processes?). In the scenario treatment, the main problem is that of completeness. Have we missed an event, a process, or a coupling of vital importance? In other nuclear technology areas, specifically reactor operation, the major surprises over the years have come from unexpected sceanarios (Windscale, Browns Ferry, Three Mile Island, Chernobyl). In geologic disposal, the problem of developing future scenarios is often postulated to be more difficult than with current technical systems - the key difference being the long timescales involved in disposal and the important rôle of natural systems. On the other hand, for repositories the technology is far less complex, the safety systems are passive rather than active and - perhaps most importantly - the continued reliance on human behaviour is minimal. Furthermore, the long-time behaviour of repositories can be compared to the very much longer-lived geological systems which can still be observed today. This is the central application of natural analogues; they provide us with a reference time frame against which the times for which our assessment models predict repository performance appear relatively short.

Uncertainties concerning the appropriateness and completeness of our scenario-hypotheses for deep repositories can thus be very much reduced by open-minded observations of natural systems. The major geological processes and events of concern (tectonic movements, hydrogeology, transport of dissolved materials in groundwater, climatic variations) all have a long and interpretable history which can be extracted from observations today.

We are therefore reasonably certain that critical or catastrophic new scenarios will not emerge; for some years now the standard scenario lists which evolved during the first half of the last decade have not altered significantly. For some existing recognized scenarios, on the other hand, significant uncertainty as to their potential impact on repository behaviour still exists. Good examples here are long-term changes in the hydrogeologic regime, flow paths in hard rock including effects of channelling, dissolution and reprecipitation, impact of colloids, effects of gases in the system.

Current uncertainties concerning scenarios, however, often relate less to their description or even quantification and more to their probability of occurrence as a function of time. Examples here are faulting, vulcanism or major changes in water table levels. A full probabilistic risk analysis requires such probability estimates and corresponding studies have been undertaken. However, even at a technical level, the residual uncertainties in estimates based largely on human judgement may remain so large, that bounding analyses indicating maximum credible consequences of such scenarios will remain of major importance. Certainly amongst the lay public, the perceived uncertainties in such long-term geological scenarios remain so high that a convincing safety case will not be built on precise numerical estimates.

These uncertainties in geological aspects of repository future scenarios are, of course, much less than the uncertainty in the future biosphere. This fact has often been used as an argument that biosphere transport and dose calculations for the far future are irrelevant in safety assessments. A more reasonable approach, however, is to recognize that dose calculations are a convenient and understandable method for illustrating the impact of radionuclides in the biosphere at any future time, to accept that these calculations are not intended as precise predictions, and to scope future extreme biosphere environments based on past evidence. In this area also natural analogues, in the sense of quantitative comparisons with natural systems, routinely play a useful rôle by allowing correlations of radioactively levels in man and in his environment and by allowing some reconstruction of past climatic conditions.

Within a given scenario, a wide variety of chemical and physical processes occur and it is important that these be adequately understood. The word "adequately" has led to some debate. One over-exaggerated viewpoint is that only those processes directly and sensitively affecting results of safety assessment need be understood. The other extreme viewpoint is that a deep scientific understanding of all processes must be sought after so that the "absolute truth" is ultimately learned. Of course, the proper approach lies in between. One beauty of quantitative safety analyses is that they help us to focus on the key processes which provide safety in the disposal system. These processes must be understood and quantified (at least in a bounding manner). Other processes which will not negatively affect safety can be treated more broadly - even if they are extremely interesting scientifically! The catch is naturally that, to be sure that the limits of our understanding are adequate for repository analyses, we must often go one step beyond the process description which is ultimately judged to be of adequate quality for a reliable system analysis.

The key processes which determine repository future behaviour are corrosion of waste matrices, mobilisation of radionuclides into deep groundwater, transport of these nuclides through the geosphere and dispersion through the biosphere. For all steps in this chain natural analogues can be found. The paper by D. Lever in the 1987 Brussels Symposium gives an interesting range of specific examples [Ref. 6]. One key question is whether the analogue is good in terms of the orginal definition by Chapman et al. [Ref. 7], in that it approximates to important repository relevant conditions. Examples of poorly chosen analogues are geochemical systems formed at very high temperatures and also systems with unreasonably long timescales (hundreds of millions of years).

QUANTIFICATION OF SYSTEM BEHAVIOUR

This involves model building and application, following collection of the corresponding input data. It is the area of safety analysis to which most effort has probably been devoted. The current consensus is that the models are generally in advance of the data. This is certainly true for structural models describing the characteristics of given sites; much specific data collection needs to be done to reduce uncertainties in site-specific databases. More challenging, however, is the fundamental question of whether today's exploration methodology allows site characterisation at a level of detail sufficient for some of the complex models proposed for use. In particular, uncertainties exist concerning our capabilities for gathering all of the data required for fracture flow models for hard rocks (such as those being developed and compared within the Stripa project) without destroying the isolation capabilities of the geologic medium. It is of importance to apply these research-type models both to assess the reliability of simpler approaches and to specify the necessary data requirements for advanced approaches.

Also for other relatively complex process models, confidence in their application can be governed by the quality of data available. Another example is water uptake and movement in unsaturated media such as in the bentonite clays in various disposal concepts or in tuff host rock. The processes can be modelled but the capillary wetting forces are difficult to quantify. Similarly, with matrix diffusion, the process model is now accepted but the governing parameters are poorly known for most rock/water/nuclide systems.

Hopes for quantitative input from natural analogue studies to safety analysis process models have risen and fallen over the years. In an initial phase, large-scale analogues like Oklo were studied in order to try and extract quantitative data on the global consequences of a repository. Valuable pointers to the retention capability of the geosphere were obtained, but the extreme age of the system and the differing geochemistry from a repository environment made direct extrapolation difficult.

Subsequently, more emphasis was placed upon analogues of specific processes. Here much has been achieved, as will be illustrated in the overview papers and in the specific Poços de Caldas reports at this meeting. Some of the critical processes for which the quantitative understanding has been improved by natural analogue studies are:

- Release from UO_2 and glass waste forms
- Solubility and speciation in aqueous solutions
- Redox front initiation and movement
- Nuclide diffusion in clays
- Matrix diffusion in fractured media
- Particulate and colloidal transport of radionuclides
- Smectite to illite transition in clays.

In all of these areas, studies with natural systems have built up, improved or confirmed our understanding, and quantitative measurements have provided data for comparing with the input or the output of our safety assessment models. In fact, most data are used in checking the credibility of models and this issue will be raised again later in the discussion of confidence building.

In summary:

- Over the past years a very extensive suite of safety assessment models has been built up covering single and coupled processes
- Application of these models has allowed us to scope the potential long-term consequences of a repository and to identify key parameters and processes
- Global analogue studies help raise confidence that important processes have not been omitted; specific analogue projects can confirm the reasonableness of model input data and the plausibility of model output predictions.

ASSESSING POSSIBLE ERRORS IN MODEL PREDICTIONS

In the above comments, we have used words like "reasonable and plausible" to describe model predictions. Such qualitative epithets are no longer alone acceptable in a technical analysis. One of the main thrusts of safety assessment at present is to try to quantify the uncerainties associated with predictions. How can this be done? Comprehensive overviews of uncertainty analysis are included in [Ref. 8] and I will extract only short excerpts of relevance here. Uncertainties arise in treatment of scenarios, in our models and in our choice of parameters and data. Some of these uncertainties are due to inherent stochastic variability in the system; for those, analysis methods have been developed and the limitation is presented rather by the difficulties in specifying input parameter distributions. Other uncertainties arise from lack of complete system understanding; these are more difficult to treat and a quantitative process to replace qualitative criteria relying heavily on human judgement does not exist.

Concerning the former tractible problems of quantifying uncertainties caused by possible data errors or variability, the current consensus in the safety community is that:

- Uncertainty analysis must be part of an overall safety assessment
- Mathematical techniques for representing data uncertainties and for uncertainty propagation through a model sequence have been developed

- A combination of deterministic (best estimate) computations, bounding analyses and probabilistic uncertainty analysis is most appropriate
- Sensitivity analysis is a separate activity which is, however, an essential precursor to full understanding of overall system uncertainty
- The uncertainties in most assessments to date are acceptable (see e.g. [Ref. 9]) in that the ranges of predicted results are not so large as to put the conclusions of assessments into question.

This last point is of very great importance, in particular when we consider the diversity of groups interested in the results of safety assessments. The PAGIS results referred to above are a good example; four different disposal options were studied and consequences with uncertainty bands were predicted. These bands are up to 3 orders of magnitude in width (other assessments have given even wider bands), but they all lie well below acceptable limits and they fall into 3 distinct groups. What can we conclude from this? A researcher might conclude that 3 orders of magnitude uncertainty (in some Swiss cases up to 10!) certainly indicate insufficient knowledge and the need for more work. A politician faced with choosing a disposal option might clutch at the lowest predictions in the hope of warding off public protest through "objective facts". A safety assessor would conclude simply that all options studied are acceptable from a safety point of view so that other criteria (costs, geographical location, public opinion, etc.) can be freely applied by the overall decision maker.

A safety assessor would also, however, question further the potential systematic errors. Such uncertainties can be due to lack of understanding and are best discussed under the topic of confidence levels of various groups; this is covered in the following section.

RAISING LEVELS OF CONFIDENCE IN SAFETY ANALYSES

The single biggest problem in waste disposal today is the widespread lack of confidence in the predictions of system behaviour into the far future. Who must have sufficient confidence? Three key groups are involved - the implementers, the regulators and the public. The ideal procedure would be for implementers to illustrate convincingly, at a technical level that the models and data are sufficient (validation), for the regulators to insist upon validation of adequate quality for licensing purposes and for both technical groups to work together in convincing decision-makers and public. Of course, their common task is to convince, not of the acceptability as such of disposal, but rather of the adequacy of the methodology providing the decision basis. We are today still far from this ideal situation of consensus in the technical community; the adversarial licensing or public hearing process in many countries compounds the obvious problems here. Confusion can result for all involved groups.

Some confusion orginates at the technical level; scientists in the field are still discussing what validation means and whether absolute validation is possible! The recent GEOVAL conference revealed the contradictory approaches. Those pure scientists who define validation as "absolute proof of correctness" will always conclude that validation is impossible. That theories can only be disproven and not proven is a long-accepted maxim in science. Adequate validation based upon a scientific consensus is the proper aim for project-specific work in which decisions on engineering options must be taken.

This consensus is strengthened by each new piece of relevant evidence which can be explained by the theory or model in question. Here is the key area in which natural analogue studies can contribute to advancing waste disposal. Only natural systems can give direct evidence of processes with the long time constants relevant for repository behaviour. Because of the value of analogue studies in model validation, they should be as carefully and rigorously planned as possible. Ability to explain or reconstruct the current status of a geological/geochemical system provides an important boost to our confidence in understanding. Even more convincing, however, is the ability to predict **in advance** relevant phenomena or parameters of the natural system. The best detailed analogue studies contain this element of "blind prediction".

With the very many analogue studies which have been carried out to date, one might expect, or hope for, a higher general level of confidence in our predictive abilities than appears to be the case. One unfortunate reason is the recurring tendency of some researchers to aim at validation beyond the specific requirements of waste disposal. A more understandable reason is that analogues are never perfect in terms of their direct relevance to repository processes and because of our imperfect knowledge of their determining boundary conditions. A more disturbing fact is that the technical community has been unable to bring the message further to other interested groups. Many technical reports on analogues have been produced for consumption by "insiders", isolated efforts (e.g. the successful Nagra brochure on analogues) have been made to produce PR material for wider usage, recently there has been a useful publication in the popular scientific press [Ref. 10] - but the interesting stories of natural analogues have not yet broken through in the wider media such as the popular press or in television.

To increase the confidence of outside groups in our safety assessment by emphasising more the contribution from natural analogues, we need to:

- continue to look for analogues of the highest quality (c.f. Chapman et al.)
- to avoid muddying the waters by selling academic irrelevant studies of natural systems under the "analogue label"
- to concentrate on issues revealed by safety analyses to be of greatest impact on repository behaviour (whilst keeping an open mind for other important processes)
- to be honest about the shortcomings of the natural analogue system studied (there are no perfect analogues!)
- to spread the work from the technical community to communicators, decision-makers and the public.

This last point is sometimes difficult for technical experts because of the required simplifications if complex explanations. Best results are obtained when professional communicators come half way to meet the technical experts.

CONCLUSIONS

In this paper, I have taken a broad view of safety analysis ranging from original build-up of system understanding through to communication of the results to all interested bodies. At each stage uncertainties arise. Although a waste disposal system is far simpler than many other technical systems analysed today, special features (such as the high dependence on natural barriers and the long timescales) necessitate the development of new approaches and techniques to reduce uncertainties in our abilities to understand and model. However, the unique boundary conditions in the waste disposal area (high levels of funding, high social/political profile) allow us to investigate, discuss and document these uncertainties at great depth. Much high quality technical work has resulted (and some wheels have been re-invented!).

Today, there is a need at the technical level to focus upon those specific uncertainties which can radically affect imminent decisions in the development of deep repositories. The experts both of implementing bodies and of regulators must be able to reach a consensus here, a consensus which allows priorities in data collection and safety analysis modelling to be set. When both parties agree that the residual levels of uncertainty are acceptable, they must both be prepared to spread this message wider. The public should ultimately be made aware and convinced of the fact that, although 100 % certainty is unattainable, a sound consensus (a wide-spread "warm tummy feeling"), based on a wealth of high quality technical work, is sufficient justification for progressing with disposal plans. Even in a politically sensitive area such as ours, we should work to ensure that societal priorities are determined as much as possible by objective, balanced judgements rather than by particular subjective pressures.

The rôle of natural analogue studies in reducing uncertainties and increasing the confidence of all interested groups is undisputed. Those at the technical level should neither become discouraged at the inherent fuzziness in our study objects nor presumtuously overconfident in our modelling abilities. The communicators amongst us should work at understanding the limitations of, and the positive evidence from, natural analogues and at spreading justifiable simplifications of the technical work to a wider audience.

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NAWG REVIEW PAPERS

DESIGN AND PERFORMANCE ASSESSMENT OF RADIOACTIVE WASTE FORMS: WHAT CAN WE LEARN FROM NATURAL ANALOGUES ?

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Summary

In this review, we specify the role of natural analogues for the development of solid radioactive waste-forms. Numerous works have been carried out on the major matrices proposed or actually in use for both high-level (glasses, spent fuel, ceramics) and low- or intermediate-level wastes (cement-based materials, bitumens, resins) as well as for metallic containers. We show that some natural, historical or archaeological materials can be considered as good analogues. We suggest that their use has been quite limited in the past for the design of matrices but that both qualitative and quantitative information of great interest (and in some cases unique) have been already inferred for assessing their long-term performance.

1.Introduction

Solid waste-forms are an important part of all multi-barriers concepts so far developed, in varied countries, for the geological disposal of nuclear wastes (Chapman and McKinley, 1987). Their principal role should be to confine the radionuclides within the repository, thus preventing any rapid leaching by circulating groundwaters and dispersion in the environment. This implies that one can guaranty the high stability of such materials in the nature, notably upon solid/liquid interactions. This goal can be partly achieved by developing materials having (thoroughly tested) high performances. However, this "materials science" approach remains insufficient when one has to consider the long-term properties of these materials (over time periods of, at least, hundreds or thousands of years) which cannot simply be assessed by laboratory testing. Within the last decade, the use of natural analogues to tackle this difficult issue has tremendously increased (Chapman et al., 1984). Indeed, a wide variety of specialists (from earth scientists, chemists and modelers to experts in safety assessment, etc.) and institutions involved in radioactive waste disposal now acknowledged the usefulness of natural analogues (see for instance Birchard, 1984 for the viewpoint of regulators).

The present paper reviews this field. My purpose was to convince that natural analogues are a key element (although not unique) of safety assessment and of confidence building in models, for both the experts and the public. Numerous studies have been carried out for a few years, with different purposes as regards radioactive waste disposal, and it would be out of the aim of the present work to be exhaustive. Rather, I tried to select major works in order to illustrate the way analogues were actually used either for design or performance assessment of solid radioactive waste matrices. Hence, this paper concentrates on near-field issues and excludes far-field ones, such as the migration of radionuclides in the geosphere, which have been dealt with in another review (Petit, 1990).

2 Types of waste-forms and available analogues

A wide variety of waste-forms has been proposed in the specialised literature, depending on the type of wastes to be solidified, the concept of disposal and the technology envisaged in each country, as well as the property of the material which is stressed (resistance to aqueous corrosion and to radiation effects, thermal capacity, etc.). Some of these materials have reached the industrial level (e.g. borosilicate glasses, spent fuel, cement-based materials) whereas others are still at a research and development stage (e.g; ceramics). A complete review of such waste-forms has been made recently by Lutze and Ewing (1988). We will consider in the present paper the following materials:

- glasses,
- spent fuel,
- ceramics (including Synroc)

which have been proposed or are actually in use for high-level wastes,

- cement-based materials,
- bitumens,
- resins,

which concern low- and intermediate-level wastes, and

- metallic containers

which are used for the encapsulation of high-level wastes (glass and spent fuel).

Several types of natural glasses have been proposed as analogues of nuclear glasses, in particular volcanic glasses (from basaltic to rhyolitic glasses) and impact glasses like tektites (Ewing, 1979; Allen, 1983). Archaeological and historical artifacts (roman glasses, stained-glass windows) have also been considered (Jantzen and Plodinec, 1984). The analogy is mainly based on the chemical composition of these materials which are all alkali and alcaline earth silicates. However, reference nuclear glasses (e.g. the R7T7 glass produced by Cogema in France) are borosilicates; boron is usually absent in natural glasses, except in small amounts in very particular sites (e.g. Macusani, Peru). Despite this striking difference, it is currently considered that basaltic glasses are quite good analogues of reference nuclear glasses, in exhibiting in particular a similar phenomenology of aqueous dissolution. Hence, most reported works concern this natural material.

Uraninite (UO_2), which is a common ore of uranium, is considered as a good analogue of the spent fuel (Haaker and Ewing, 1980). Major differences originate from intense radiation effects and the presence of high amounts of fission products and transuranium elements in the latter. However, in the uranium mine of Oklo (Gabon) natural nuclear reactors that have functioned about 2 billion years ago have produced features very similar to those of the technological material, and uraninite from this site is thus an excellent analogue (see for instance Cowan, 1978; Hageman and Roth, 1978).

Many natural minerals can be considered as good analogues of ceramics constituents (Haaker and Ewing, 1980 and 1981). Indeed, they usually have comparable chemical compositions and crystallographic structures, and contain a similar spectrum of certain trace elements such as lanthanides and actinides (U and Th and their decay products). For instance, the constituents of Synroc, for "synthetic rock", a polycrystalline ceramic first proposed by Ringwood in 1979 (see for instance, for a review on this ceramic, Ringwood et al., 1988) at the Australian National University are found in nature, namely zirconolite, perovskite, hollandite, titanium oxide and pyrochlore structures. Monazite and sphene, two ceramics developed respectively by Boatner and Sales (1988) at ORNL (USA) and Hayward (1988) at AECL/Whiteshell (Canada), are also natural minerals for which a direct analogy is thus possible.

Several historical and archaeological cements (notably roman and gallo-roman cements) have been studied as analogues of cement-based matrices (Jull and Lees, 1990). Although most of these materials have been made with a different technology than that used nowadays, similar constituents (hydrated calcium silicates, ettringite, etc.) can be found in some locations, where specific ingredients have been used and/or particular conservation conditions have occurred.

Natural bitumens, and archaeological artifacts made up of such organic matters, have been recently investigated as analogues of technological bitumens (Helmuth, 1989a and 1989b). The analogy seems good from both the chemical composition and molecular structure viewpoints.

Natural resins (e.g. amber) have been proposed as analogues of thermosetting resins but no detailed work has been done yet and the analogy appears, in any way, quite limited (Helmuth, 1989b).

Finally, native metals as well as archaeological and historical artifacts appear as very convincing analogues of their technological counterparts used for containers, notably in the case of iron and copper (Chapman et al., 1984; Hallberg et al., 1987).

In the following two sections, we will first try to identify whether natural analogues have actually been used by scientists and engineers for **designing** waste-forms. We will then deal with the **evaluation of properties** and **performance assessment** of these materials.

3. Role of natural analogues in the design of waste forms

In the past, the use of natural analogues for design has been variable depending on the type of waste matrix. On can consider that analogues played no major role (if any) for glasses, spent fuel and cement-based materials. Some vague reference to obsidians, in earlier works, as an indication of the likely high durability of nuclear glasses, does not demonstrate any active role on design. Another proof is given by the fact that glasses of varied compositions have been initially proposed and developed, where no analogy of any kind was possible with natural materials (e.g. phosphate glasses; Sales and Boatner, 1988) (see for a review on glass Lutze, 1988). Indeed, political options for waste management, engineering ideas and technological constraints, which are quite strong in this field, have obviously been dominant. In particular, the choice of glass or spent fuel only reflects the option of reprocessing or not the high-level wastes produced in nuclear reactors. The formulae of cement-based materials for various low- and intermediate-level wastes have obviously been proposed on the basis of current cement technology with no particular reference to ancient binders. Indeed, it is only when one strengthens the importance of the long-term behaviour of such materials that one has to rely on natural analogues. The role of the latter is thus posterior to the development and the technological use of these materials and played no role in their initial design.

On the contrary, promoters of various ceramics (notably Synroc, monazite and sphene) have explicitely made reference to natural analogues as the generating idea for the design of these materials (Ringwood et al., 1988; Boatner and Sales, 1988; Hayward, 1988). The starting point of these authors was indeed to search in nature for minerals which would be able to incorporate, in sufficient amounts, fission products and actinides and to exhibit a demonstrated long-term resistance to radiation effects and to aqueous corrosion, in a variety of natural systems. The influence of natural analogues in the initial design of those ceramics is thus very clear. The precise making of these materials and their development for varied types of wastes depended on current technologies. It was also stated that this procedure for designing a high-level waste-form would greatly help convince the public (and safety authorities) of the appropriateness of the chosen approach, in particular as regards the long-term performance of such confinement matrices.

In the future, however, the role of natural analogues, which now constitute a soundly-based field of study, could be much greater in the design of waste-forms. The evaluation of their likely long-term behaviour, considered as a key issue of safety assessment, could be the starting point for any improvement of existing matrices or, even, for the design of entirely new ones. Indeed, the idea of developing the so-called "high temperature" silicate glasses, which would have an increased content in network formers (notably SiO_2 and Al_2O_3) and thus a much higher stability towards aqueous corrosion, derives, at least partly, from the observation that rhyolitic glasses (average SiO_2: 70-75%) are much more durable than basaltic ones (SiO_2: 45-50%), in a wide variety of environments (see for instance Ericson, 1981; Zhou et al., 1987; Magonthier et al., 1990).

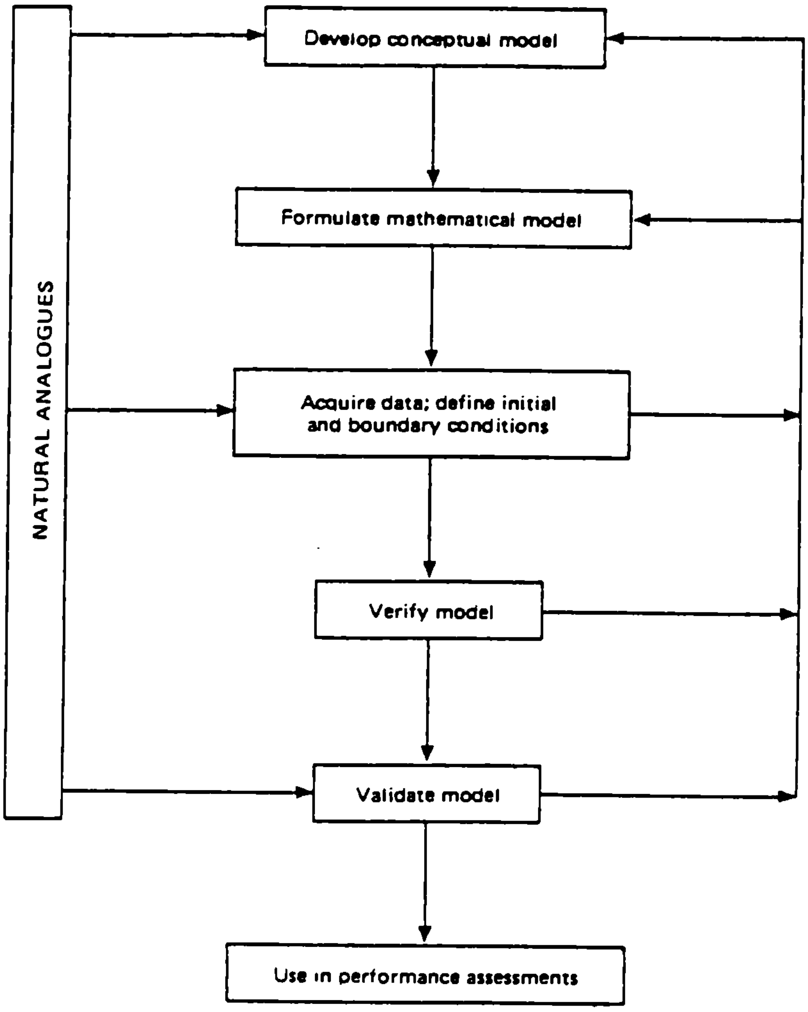

Figure 1: Role of natural analogues in developing and validation models (from IAEA, 1989).

4. Role of natural analogues in the performance assessment of waste-forms

A recent panel of experts (IAEA, 1989) has acknowledged the role of natural analogues, from both qualitative and quantitative viewpoints, in performance assessment. Three main areas have been identified (figure 1):

* development of conceptual models. In the case of waste-forms, this would include for instance a model of aqueous dissolution: how thermodynamic and/or kinetics aspects should be introduced in the model ? what are the main processes to consider (e.g. hydrolysis, ion exchange, redox reactions), etc.? This first step is fundamental since it controls the global structure of the model and the hierarchy of mechanisms and processes involved. The role of natural

analogues is essential, and unique for long-term issues, in this qualitative activity.

* acquisition of data, definition of initial and boundary conditions. This also important for properly running a proposed model. Analogues can be useful in this area, despite the fact that data are often difficult to extract from such natural sites, precisely because initial and/or boundary conditions are hard to estimate in the environment over geologic time spans. This is a qualitative and quali-quantitative activity, respectively.

* validation of models. This is a fundamental step when scientists want to convince themselves (and hence authorities and the lay public) that the model developed is pertinent and gives credible predictions of what should occur in a repository. For the long-term, natural analogues are here irreplaceable. Validation can be qualitative or quantitative. Orders of magnitude in the evaluation of the outputs of a model can be sufficient since, in safety assessment, one is merely interested in fixing upper limits.

The features of waste-forms which are of interest in performance assessment are essentially those leading to a variability of their properties with time. The latter can be classified into chemical, thermal, mechanical and radiative ones. In particular, the alteration of the matrix (including aqueous dissolution or more complex phenomena), the leaching of radionuclides and the corrosion of containers are key issues. For glass, the devitrification has also to be considered because, then, a basic property of the matrix (its amorphous nature and the corresponding homogeneous distribution of radionuclides) would be drastically modified. Crystallisation can affect silicate or oxyhydroxide gels which are likely to form during the alteration of matrices. Thermal phenomena can also lead to the so-called Soret effect (thermo-diffusion). Mechanical phenomena include in particular the fracturing of waste-forms which increases the surface area potentially exposed to water attack. Radiative effects can affect other properties of waste-forms: radiation-induced dissolution and diffusion, solid and/or liquid radiolysis (and its possible feedback on matrix dissolution) are for instance well known. Since solid/liquid interactions are likely of major significance for the long-term behaviour of waste-forms, the properties of the solution should also be considered in any modeling. This includes the redox potential and pH, the solubility and speciation of radionuclides, the presence of colloids and the activity of micro-organisms.

Reasoning by analogy is a methodology which needs to be carefully mastered. I have shown recently (Petit, 1990), on the basis of studies in the history and sociology of science, that it plays a major role in scientific discoveries, in particular in its psychological and cognitive aspects. In fact, apart from induction and deduction on which normal scientific "demonstrations" are based, analogy is a very common and powerful mental process for tentatively deriving the unknown from the known, in a dialectic manner, which needs, of course, to be subsequently validated.

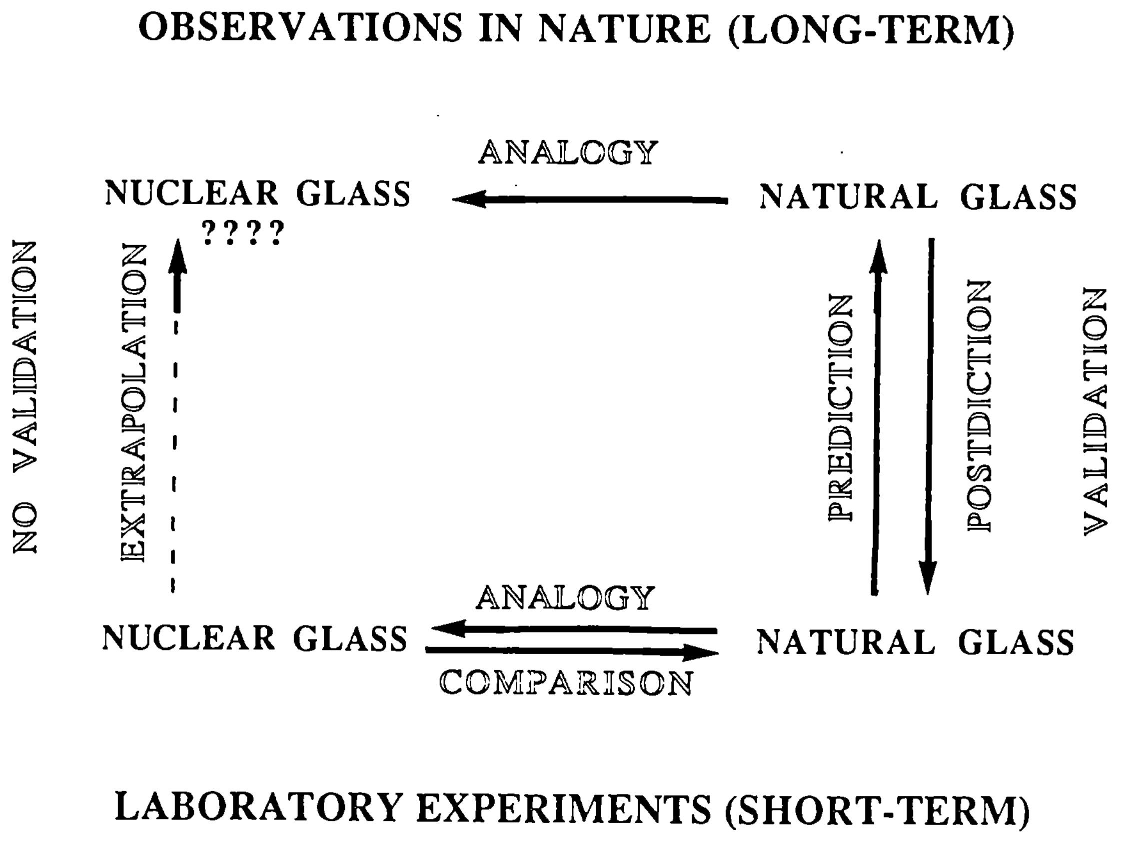

Figure 2: Reasoning by analogy: a methodology schematized here in the case of glass dissolution.

Figure 2 illustrates this methodology in the case of nuclear glass dissolution. What we are interested in is to extrapolate short-term laboratory experiments on the nuclear glass to long-term environmental conditions (within the repository). This is not possible in the framework of a normal scientific approach because no direct validation of these extrapolations is accessible. However, natural analogues constitutes an indirect means to get confidence in the model used for such an extrapolation. In effect in short-term laboratory experiments, the behaviours of a nuclear glass and its natural counterpart can be compared. The analogy between dissolution features, and its implication for involved mechanisms, can be fully analysed. A model of glass dissolution, valid for both glasses at the laboratory scale, can be developed. Then, by observing natural samples corroded in the environment (for long periods of time, in complex conditions and at large dimentional scales), one can proceed to two indispensable exercices: firstly, to "postdict" (according to the definition of Ewing and Jercinovic, 1987) what should be the initial and boundary conditions on the short-term, by assuming a given behaviour (one should for instance correctly attribute observed features to aqueous dissolution and not to any other phenomenon). The validity of such postdictions can be checked by comparing them with laboratory results. If it does not fit our expectations, one can then question one's basic assumptions. Secondly, by using laboratory data and by assuming a given model of glass dissolution one can predict what should be the long-term effects, which can be tested on the natural system. This process is simply validation. In turn, one can have a reasonable confidence in a model which would be sufficiently general to account for short-term behaviours, on both nuclear and natural glasses, as well as for long-term evolutions observed on natural samples. This model can finally be applied to predict the long-term dissolution behaviour of the nuclear glass.

We will now show that, for all the issues identified above and following this methodology, natural analogues can give useful, and in some cases unique, information.

5. Overview of findings from natural analogues

Such studies include both observations made on natural samples, experimentations conducted in the laboratory on natural (or even simulated) samples and modeling. For sake of clarity, the main results presented here have been classified in order to show how they can contribute to the three items cited above, namely development of a conceptual model, data acquisition and definition of initial/boundary conditions, and finally validation of models. Concerning the first two items for aqueous dissolution, we will try in each case to answer 6 basic questions, following the suggestion of Lutze (1988) made for glass:

- what is the mechanism ?
- what is its rate ?
- is there a change of mechanism with time ?
- what is the influence of environmental parameters ?
- what are the alteration products and their sequence of

formation ?
- what is the behaviour of elements of importance for safety assessment and notably trace/minor elements, during dissolution.

5. 1 Glass

Numerous analogue studies have been reported on glass, particularly on basaltic glasses from various sites (Iceland, Red Sea, Japan, etc.) and more punctually on rhyodacitic and rhyolitic glasses (Iceland). Most early investigations concerned the alteration of basaltic glass in sea water (this material is in fact produced at mid-ocean ridges) but more recent ones dealt with its alteration by sub-glacial waters, thence in conditions closer to those expectable in a continental repository (Ericson, 1981; Allen, 1983; Crovisier et al., 1986; Zhou et al., 1987; Crovisier et al., 1987; Arai et al., 1989; Crovisier et al., 1989 and 1990). Much work has been devoted to validate the analogy itself, first suggested by Ewing (1979), based on the similarity of chemical composition (again at the exception of boron and aluminum) between nuclear and natural glasses. Most work dealt with dissolution because Ewing demonstrated in this early work that devitrification would not probably be an issue for periods of times inferior to 1 million years.

Two main lines of research have been explored:

* from a pure phenomenological point of view, Lutze et al. (1985), for instance, showed that a borosilicate nuclear glass and a basaltic one leached in a saturated synthetic NaCl solution at 200°C exhibited amazingly similar alteration features (figure 3). In particular, the morphology of the hydrated rind that forms at the solid/liquid interface is multilayered and cubic analcime crystals forms on top of it in both cases. Many other studies have demonstrated that such an hydrated rind (called "palagonite" for basaltic glass leached in sea water) is characterised, for both nuclear and natural glasses, by a depletion of Na, K, Si, Mg and Ca, a marked enrichment in U, Th, REE, transuranic elements, Ti, Fe, etc., and a variable concentration of Al, depending on pH, but which however remains often constant (see for instance Barkatt et al., 1986; Bunker, 1987; Crovisier et al., 1987; Crovisier et al., 1990; Petit et al., 1989; Murakami et al., 1989; Jercinovic et al., 1990; Magonthier et al., 1990; Petit et al., 1990; Vernaz and Dussossoy, 1990).

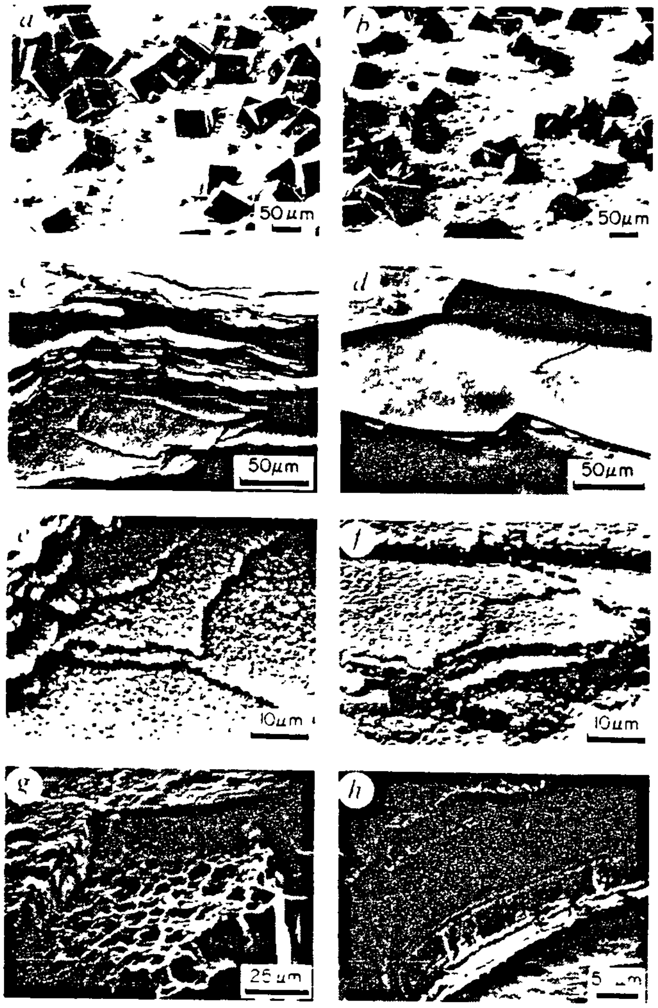

Figure 3: Analogy between the alteration features (SEM micrographs) of a basaltic (a, c, e) and a borosilicate nuclear glass (b, d, f) leached 30 days in a synthetic NaCl brine at 200°C. Dredge sample of basalt glass (g, h) altered in sea water at 3°C (from Lutze et al., 1985).

On this topic, laboratory experiments conducted on these two types of glasses have had major ouputs for the identification of the dissolution mechanisms. For instance, Petit et al. (1990) have shown by means of resonant nuclear reaction analysis (RNRA) that the marked hydration of a nuclear glass during leaching in deionised water is counterbalanced by a superficial release of sodium (figure 4) When leached in a saturated sodium brine, one notes that both hydration and alkali depletion are hindered; one can even notice some penetration of sodium in the outermost region of the glass. This demonstrates that one of the first mechanism of glass corrosion is ion exchange between a species of hydrogen and mobile

mobile network modifiers (mainly Na, Li, Cs for the R7T7 glass). Studies along the same line have demonstrated the occurrence of other concurrent mechanisms, namely network hydrolysis and repolymerisation, permeation of water molecules, etc. The Rutherford backscattering spectrometry (RBS) applied to the same glass shows (figure 5) that such an alteration is accompanied by some superficial depletion of silicon and by the accumulation of various heavy elements, namely transition elements (notably iron),

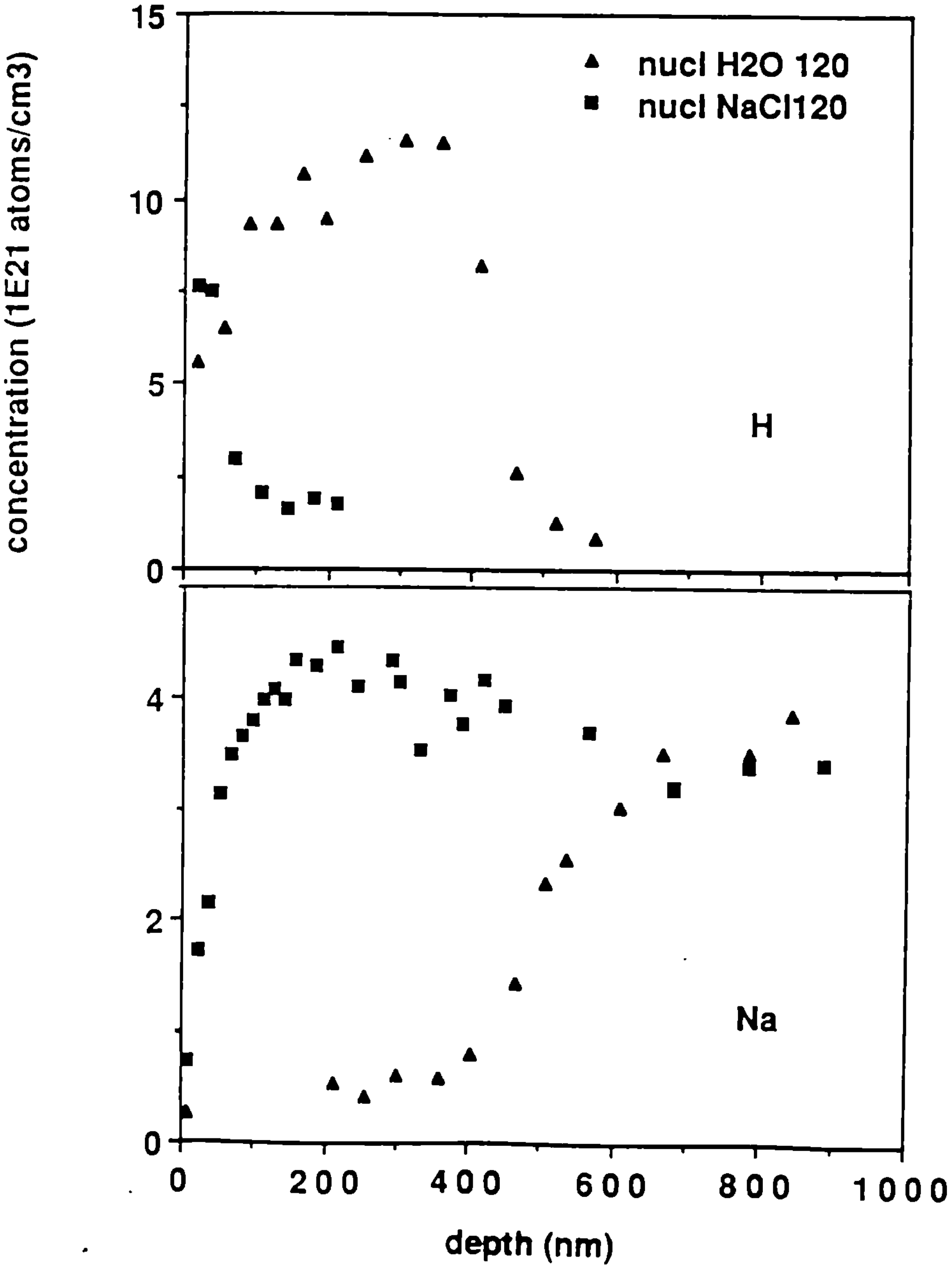

Figure 4: Hydrogen and sodium depth profiles obtaines by RNRA on the nuclear glass R7T7 leached 13 hours at 120°C (from Petit et al., 1990a).

lanthanides and actinides. Very analogous mechanisms can be observed with the same techniques on both the basaltic and rhyolitic glasses, hence demonstrating the good phenomenological analogy between all three glasses, in spite of notable differences in chemical composition (see for instance figure 6 and 7 for the basaltic glass).

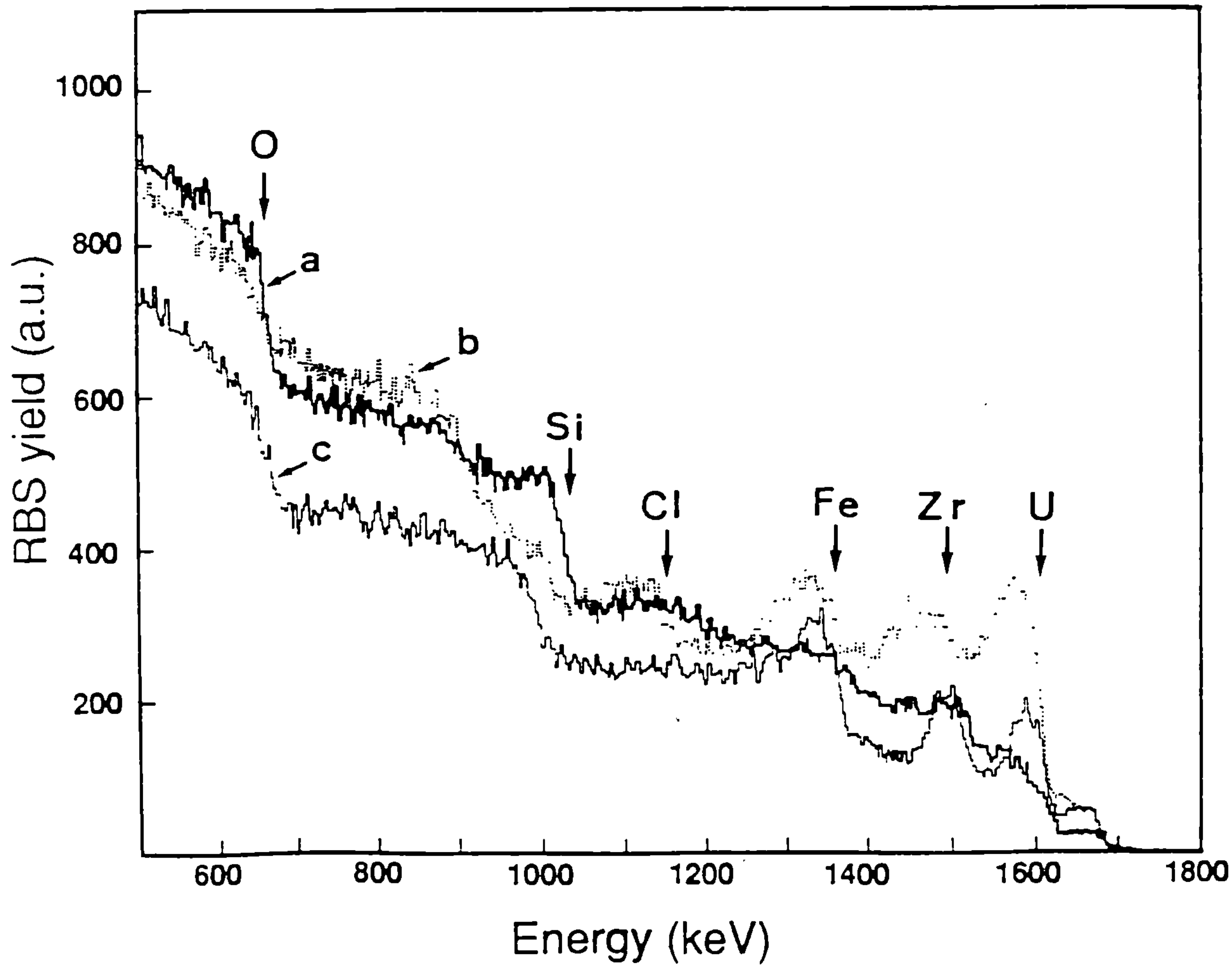

Figure 5: RBS spectra of the nuclear glass R7T7 untreated (a) or leached 13 hours at 120°C in deionised water (b) or a NaCl brine (c) (from Petit et al., 1990a).

Long-term rates of natural glass alteration have been estimated by measuring the thickness of the hydration rind versus time (Grambow et al., 1986). Although criticisms can be raised against such measurements (time of water attack poorly known, rind thickness possibly not directly linked to rate of alteration, etc.), such a work shows first that quantitative data of reasonable value (at least orders of magnitude) can be inferred from analogues and second that the apparent rate varies notably according to the local geochemical conditions. For instance in the case of basaltic glasses leached by sea water at the bottom of oceans (low temperature), rates of 3-20 µm/1000 years have been estimated in low-silica conditions, of 0.1 µm/1000 years in high-silica conditions and of almost zero when silica reaches saturation as a result of the sealing of the system by the formation of secondary authigenic minerals. Such ranges of alteration rates are confirmed by other works, where the environmental conditions (water composition, flow, temperature, etc.) have also been thoroughly determined (see for instance Arai et al., 1989).

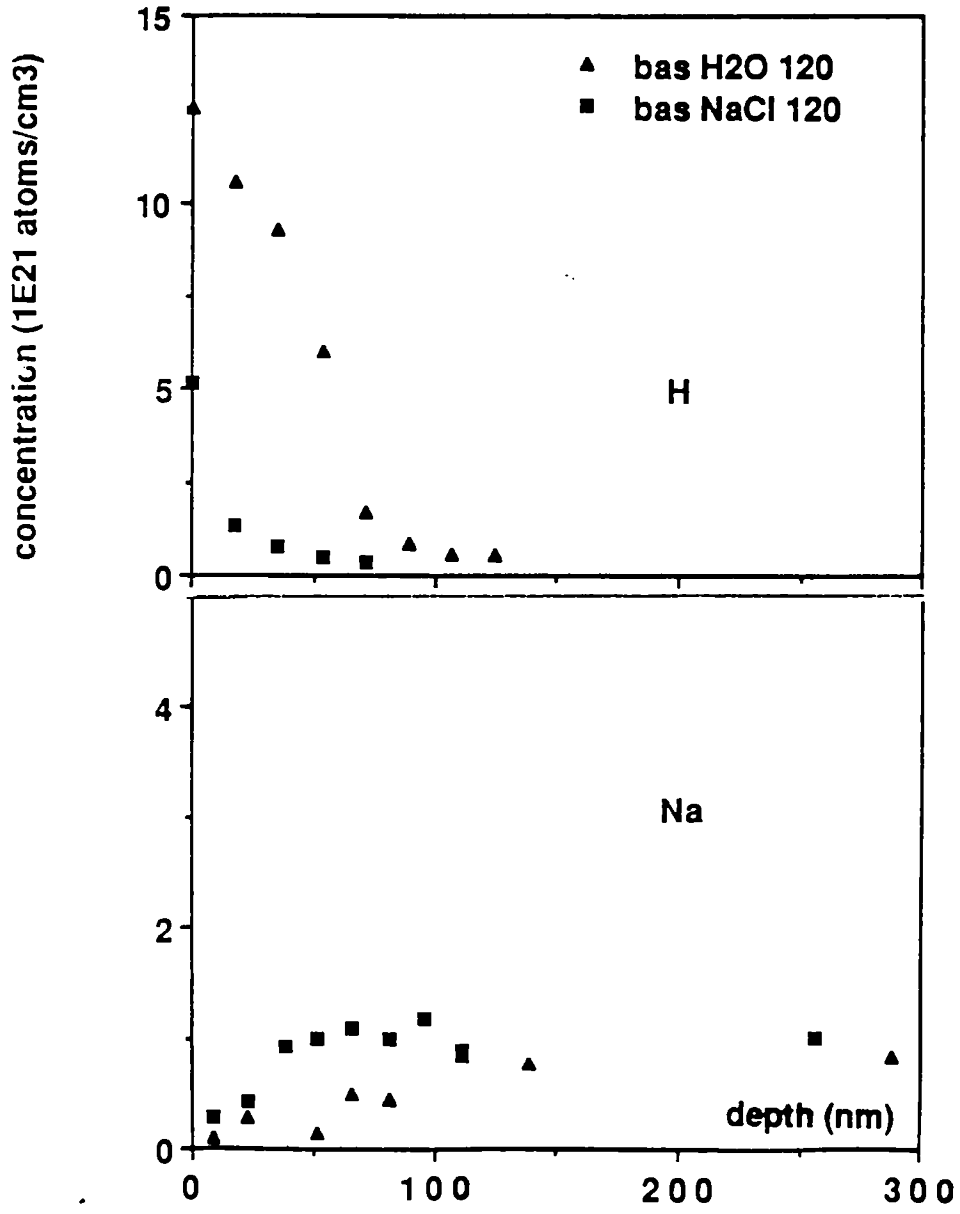

Figure 6: Hydrogen and sodium depth profiles obtaines by RNRA on the basaltic glass R7T7 leached 13 hours at 120°C (from Petit et al., 1990a).

Numerous measurements of alteration rates have been made in the laboratory on both natural and, mainly, nuclear glasses (Murakami et al., 1989; Jercinovic et al., 1990; Petit et al., 1990). It is not the place here to recall all these data, but it is worth mentioning that they show a good similarity of behaviour between basaltic and nuclear glasses and a trend of markedly decreasing rate with time. In particular, the possible existence of a so-called "residual affinity" on the long-term has been postulated by Grambow (1984), on the basis of laboratory experiments. It would

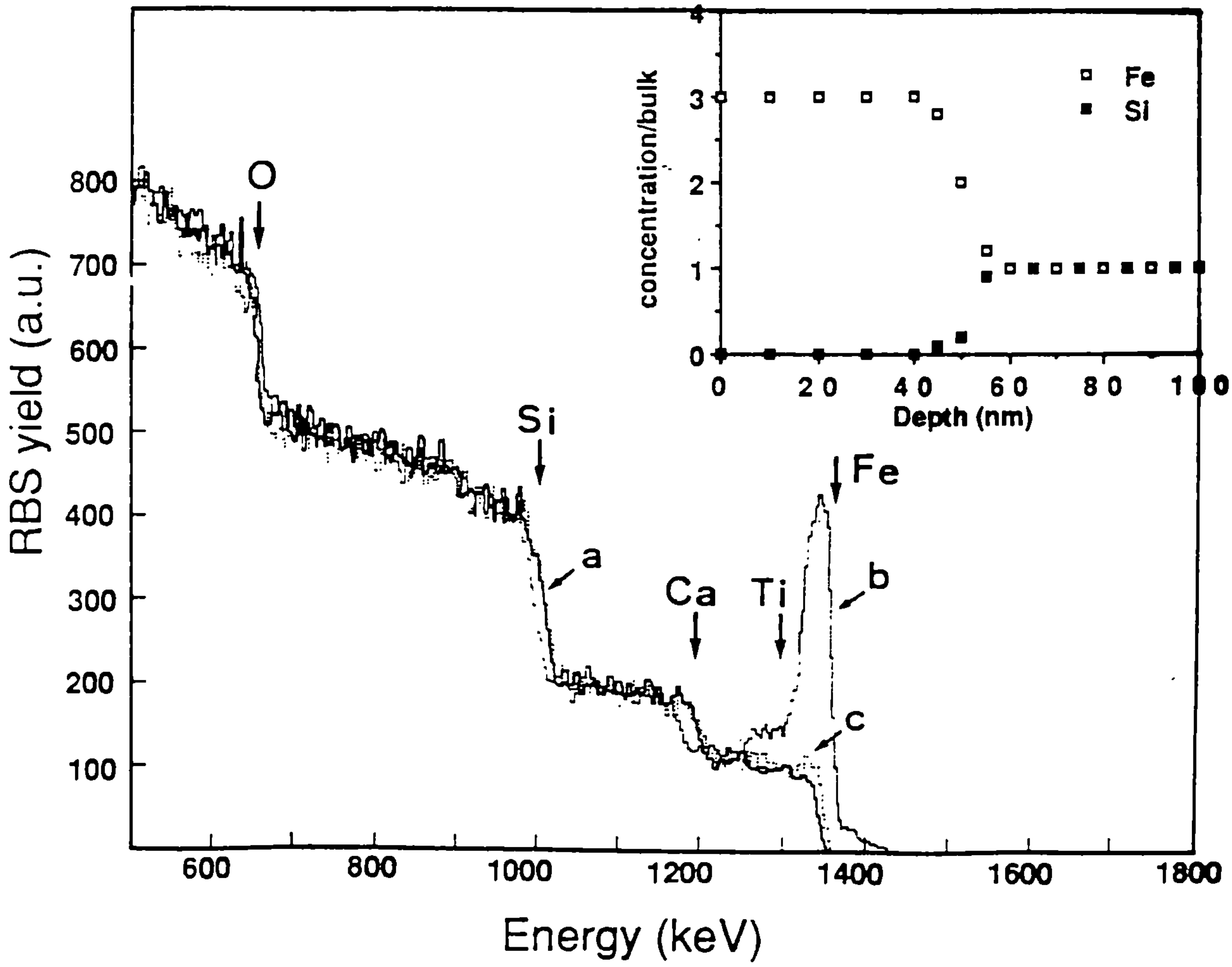

Figure 7: RBS spectra of the basaltic glass untreated (a) or leached 13 hours at 120°C in deionised water (b) or a NaCl brine (c) The insert illustrates a deconvolution of the RBS spectrum, strongly suggesting the formation of a iron hydroxide during dissolution (from Petit et al., 1990a).

originate from the fact that silicate glasses being metastable substances cannot but continue on dissolving on the long run until totally transformed into more stable secondary products (clay minerals, (oxi)hydroxides, zeolites, etc.). However, experiments are still unconclusive on this matter (see for instance Petit et al., 1990) and analogues seem to be here of limited help.

The possible change of dissolution mechanism with time is still a debatable question. However, indications from both laboratory and environmental observations lead us to think that it mainly depends on the solid/solution system. For instance for basaltic glasses, the results of Crovisier et al. (1987, 1990) strongly suggest that the stoichiometric dissolution of the glass (network hydrolysis) is the rate ruling mechanism for both short- and long-terms in sea and deionised waters (with the exception of some H-Na ion exchange occurring on the very short-term in the latter solution). On the contrary for rhyolitic glasses, evidences exist to suggest that diffusion through the alteration rind and/or precipitation of secondary minerals could be rate-controlling on the long-term (Magonthier et al., 1990). Grambow (1984), who based his first modelings on the stoichiometric dissolution of the glass did in fact introduce more recently diffusion through the hydrated layer to better account for his experimental results. It is thus possible that the rate-ruling mechanism will change on the long-term for nuclear glasses too, but natural analogues help find out what are the possibilities on which our modeling of glass/water interaction should be based.

Several environmental parameters have been shown to play an essential role on glass dissolution, notably for the long-term, on the basis of natural analogue studies (Grambow et al., 1986; Crovisier et al., 1987; Magonthier et al., 1990). Temperature appears of course of paramount importance. Investigations have been conducted on samples altered in the range 0 - >100°C. It has been shown that, around 100°C, basaltic glasses alter at a rate of 3 µm/year (a value possibly extrapolable to nuclear glasses in similar conditions) and that this rate increases by a factor of two every 12°C. The latter estimation is indeed very close to measurements obtained on nuclear glasses (about a factor 2 every 10°C), which confirms that these glasses have similar activation energies of alteration (see below). The pH is also a major parameter which governs, the stoichiometry of the dissolution process, its rate, the nature of alteration products, and the behaviour of aluminum, as already mentioned. As laboratory experiments, analogues show that both the surface area of glass upon volume of solution (SA/V) and the flow rate are major parameters. Indeed, the dissolution rate increases markedly when the flow rate increases and when the SA/V ratio decreases. Finally, the composition of the solution is important, in particular the concentration of silicon (see above), which seems to be rate-controlling, and the concentration of alkalis, notably in the case of sea water.

The alteration products have also been studied in detail on both basaltic, rhyolitic and nuclear glasses in a wide range of conditions (Arai et al., 1989; Cowan and Ewing, 1989; Crovisier et aL., 1990). Numerous minerals and poorly organised compounds (e.g. hydrosilicate and hydroxide gels) have been identified but it is remarkable to note that they can all be classified in a limited number of categories, namely carbonates, clay minerals and zeolites. In addition, the comparison of laboratory and environmental observations have allowed the identification of metastable phases (e.g. hydroxicarbonates), which therefore should not be considered in long-term modelings (Crovisier et al.., 1986). Finally the testing the predictions of geochemical modeling against analogues permitted to specify some minerals which, despite their thermodynamic stability, are kinetically hindered (low rate of formation).

Analogues confirm the behaviour of elements of interest for safety during glass dissolution, as initially deduced from laboratory experiments, and have also helped identify a mechanism which was first overlooked. Indeed, such samples demonstrate the long term accumulation of most heavy elements (transition elements, lanthanides and actinides) within the altered layer (Jercinovic et al., 1990; Petit et al., 1990). Since a good analogy between such elements and their artificial counterparts can be postulated (see for instance Chapman et al. , 1984), one can extrapolate the likely long-term behaviour of the latter on a quite firm basis. However, one has also observed the selective release of certain heavy elements while hydrated layers crystallise with time. This phenomenon is still very poorly known, in particular from a kinetic viewpoint, but one can, in effect, suspect that amorphous gels will tend to organise with time and eventually transform into stable crystalline compounds. It has been observed (Magonthier et al., 1990) that iron and titanium both accumulate in hydrated layers but that only the former element is retained whenever clays form (e.g. iron smectites). On the contrary, the latter element is completely lost into the solution because.it cannot seemingly be incorporated into the lattice of such minerals. This phenomenon, which was not previously taken into account, could be of great importance for some radionuclides, in suggesting that the accumulation of actinides in the hydrated layer, which is very favorable to safety, may be transitory.

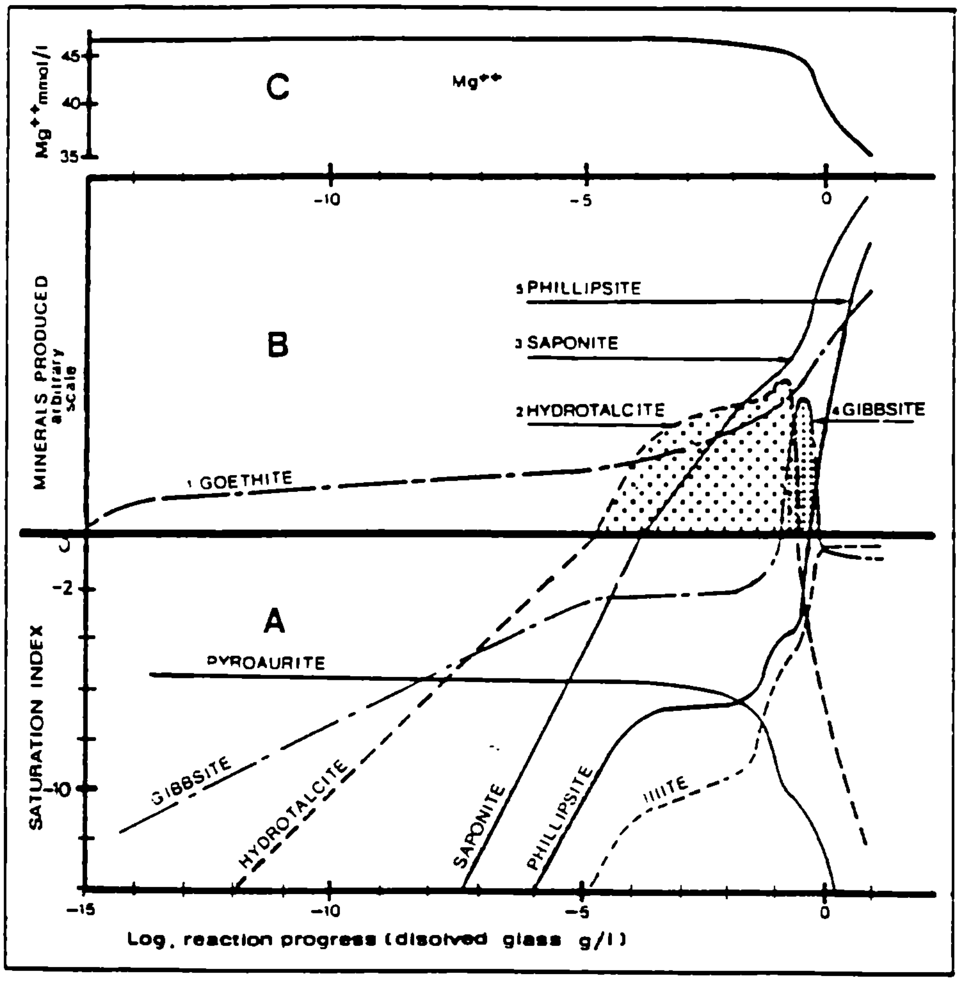

Figure 8: Geochemical modeling by DISSOL of the basaltic glass/sea water interaction at low temperature (from Crovisier et al., 1986).

The validation of models is a topic where analogues have already demonstrated their great usefulness, in particular for geochemical modelings. Indeed, several computer codes have been used (EQ3/6, PHREEQUE, DISSOL) to model the evolution of the glass/solution system with the degree of reaction, i.e. with time. Such codes are founded on the three following basic hypotheses:

- the dissolution of the glass is assumed to be stoichiometric,
- a reversible, global and instanstaneous equilibrium is postulated within the system,
- secondary phases (crystalline and/or amorphous) form when their solubility limits are reached in solution.

Although, kinetic options can be introduced in such codes either directly or indirectly (e.g. the rate of glass dissolution), they can be considered basically as thermodynamic modelings.

Environmental alterations of natural glasses (mainly basaltic glasses) have been simulated by such geochemical codes in different systems (see for instance Crovisier et al., 1986, 1989, 1990). A remarkable conclusion of these works is that, in sea and sub-glacial waters, both the nature of secondary phases and their sequence of occurrence with the degree of reaction can be conveniently simulated. Despite limitations of this approach (important constraints applied to the solid/liquid system are arbitrarily chosen) such a result can be considered as a validation of geochemical models, and hence of their basic assumptions. An example of computer code predictions is given in figure 8 which shows, in the case of basaltic glass alteration in sea water, a sequence of secondary minerals (goethite, hydrotalcite, saponite and eventually philippsite) which are actually observed either in laboratory experiments (first two compounds at short-term) or in nature (last two, on the long-term).

* from a thermodynamic point of view, the approach proposed by Paul (1977), and developed for our purpose by Jantzen and Plodinec (1984), has also given interesting results. In this model, Paul tries to relate the durability of a glass ("weighted" by the release of a constituent element such as Si or an alkali) to an intrinsic thermodynamic parameter like the free energy of hydrolysis. This last mechanism is assumed to be dominant but any other reaction could lead to the same treatment in this model, provided the corresponding thermodynamic data are available. Since glass is a metastable material, this parameter is unknown and cannot even be clearly defined. Paul suggests (and this is the trick of his model) to consider the glass as a solid solution of structural units (e.g. calcium metasilicate, silica, iron oxide, etc.) to which known free energies of hydrolysis can be assigned. The "mean free energy of hydrolysis of the glass" is then defined as the sum of these individual quantities weighted by the concentration of each type of structural unit in the glass. Jantzen and Plodinec (1984) applied this method to a wide range of glasses, both technological (including nuclear), natural, historical and archaeological glasses (figure 9). This approach offers the possibility to rank glasses of different compositions with reference to a common parameter that can be easily evaluated. The durability of the nuclear glass can then be estimated with respect to that of glasses of supposedly known durabilities. This work shows that nuclear glasses are thermodynamically close to basaltic glasses and should therefore have comparable durabilities in similar environmental conditions. It also suggests that the durability of high-silica containing glasses (e.g. rhyolitic glasses) should give an upper limit of the durability of nuclear glasses.

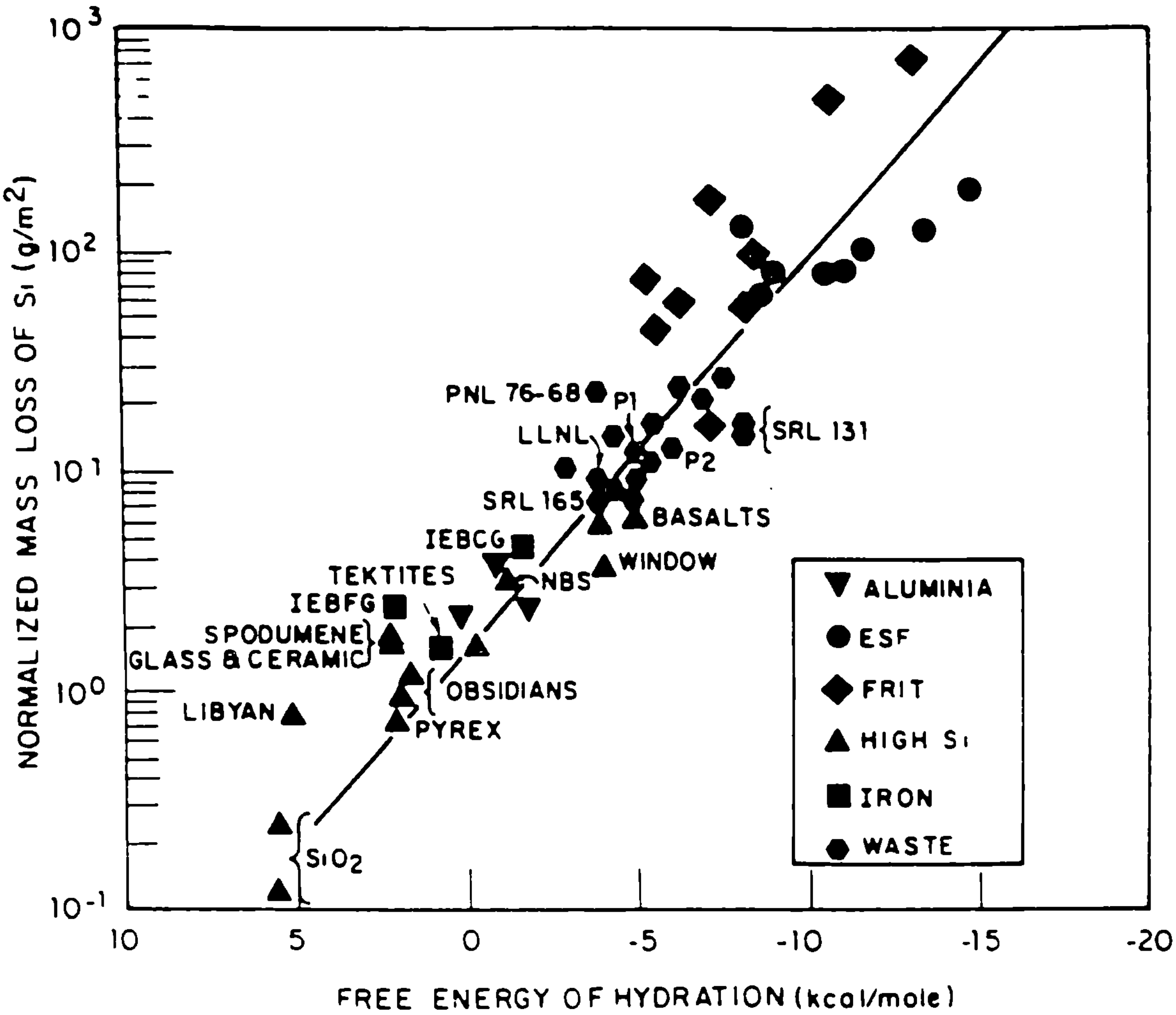

Figure 9: Rate of silica release for various natural, technological and nuclear glasses as a function of their calculated mean free energy of hydration (from Jantzen and Plodinec, 1984)

Other phenomena, of importance for nuclear glasses, have not been addressed by means of natural analogues (radiation effects, fracturing, etc.). In particular natural glasses contain too small amounts of alpha emitting elements (U and/or Th concentrations are in the range 1-30 ppm) to allow any inference of long-term radiation effects in such materials.

5.2 Spent fuel

Most analogue work in this field also deals with the dissolution behaviour (for a review on spent fuel see Johnson and Shoesmith, 1988).

Concerning the development of a conceptual model, data acquisition and definition of initial/boundary conditions the main results are as follows. Mechanisms of spent fuel alteration have essentially been identified through laboratory experiments conducted on pure UO_2 samples (Bruno et al., 1986; Wang and Katayama, 1981; Lahalle et al., 1989; Sunder et al., 1989). Detailed surface analysis, notably by XPS, of leached uraninite (the mineral constituent of the spent fuel) as well as the study of solution speciation have demonstrated that redox reactions play a central role in its dissolution. The fugacity of oxygen should thus be a major geochemical parameter of the system.

The rate of dissolution hence markedly increases with the oxygen dissolved in solution, but also with the carbonate concentration. This is due to the formation, in oxidising conditions, of very stable carbonate complexes of the uranyl cation such as $(UO_2(CO_3)_2)^{2-}$ and $(UO_2(CO_3)_3)^{4-}$. Analogues suggest that a similar phenomenon occur with other strong ligands commonly present in nature such as phosphate, fluoride and chloride.

Unfortunately, there is almost no information yet on the possible change of dissolution mechanism with time but through the indications given above, it seems quite unlikely.

Among environmental parameters which can influence the dissolution of uraninite, we have already stressed the major role of the redox potential. In fact, it is well known through natural analogues that this mineral is highly unstable, and dissolves very quickly, in oxidising conditions whereas it is a quite stable compound in reducing ones, to which most of the known ore bodies are associated. Some ores have indeed survived without notable alteration for periods greater than 1 billion years such as at Oklo (Gabon) or Cigar Lake (Canada)(Cramer, 1989). The high stability of uraninite in reducing conditions is attributable to the very low solubility of U(IV) which is $< 1\ 10^{-9}$ M/kg (Bruno et al., 1986). In the case of Cigar Lake a remarkable consequence is that, despite the huge amounts of uraninite "disposed" at a depth of about 500 m, no uranium anomaly has been detected at the earth surface. Similarly, the high unstability of uraninite in oxidising conditions is due to the high solubility of U(VI) which is $> 1\ 10^{-5}$ M/kg. Again, strong ligands (e.g. carbonates) can play an important role for increasing the solubility of uranium.

Few studies have been dedicated to the alteration products of uraninite but a recent work by Finch and Ewing (1990), conducted on samples from the Shinkolobwe mine (Central Africa), is extremely encouraging. In oxidising conditions, they observed that alteration minerals are numerous (about 50) but are essentially constituted of oxide hydrates and silicates (many of them being quite "exotic", see table 1). These authors could also reconstruct the sequence of their formation in great detail as well as the behaviour of many minor elements during alteration. Basically, uraninite which initially contains U(IV and VI), Pb and La first transform into Pb-U oxide hydrates which incorporate U(VI), Ca, Pb, K, Na, Si, Ba. Apart from the oxidation of uranium atoms one notes an input of elements from the leaching solution (alkalis, alcaline earths and silicon). Whenever silicon is present in solution in sufficient concentrations, uranyl silicates then precipitate, containing U(VI), Ca, Si, K, Na and Pb. These should thus be the long-term stable phases to take into account in similar conditions. The precise crystallographical mechanism of this mineral transformation could even be specified.

OXIDE HYDRATES	
schoepite*	$UO_3 \cdot 2H_2O$
rutherfordine	UO_2CO_3
becquerelite	$Ca(UO_2)_6O_4(OH)_6 \cdot H_2O$
billietite	$Ba(UO_2)_6O_4(OH)_6 \cdot 8H_2O$
compriegnacite	$K_2(UO_2)_6O_4(OH)_6 \cdot 8H_2O$
clarkeite	$(Na,Ca,Pb)U_2(O,OH)_7$
curite	$Pb_2U_5O_{17} \cdot 4H_2O$
fourmarierite	$PbU_4O_{13} \cdot 6H_2O$
masuyite	$Pb_3U_8O_{27} \cdot 10H_2O$
vandendriesscheite	$PbU_7O_{22} \cdot 22H_2O$
SILICATES	
uranophane	$(H_3O)_2Ca(UO_2)_2(SiO_4)_2 \cdot 3H_2O$
cuprosklodowskite	$(H_3O)_2Cu(UO_2)_2(SiO_4)_2 \cdot 4H_2O$

*The phase α-$UO_3 \cdot 0.8H_2O$ is assumed to be dehydrated schoepite (Hoekstra and Siegel[8]).

Table 1: Uranyl minerals identified at Shinkolobwe, Zaire (from Finch and Ewing, 1989).

The behaviour of elements important for safety can be inferred from various analogue studies but is best illustrated by the work done at Oklo, in the framework of the Franceville project. The fate of numerous fission products and actinides has been specified through the analysis of the isotopic spectra of their daughters. Of course, each elements exhibits its own geochemistry but main categories of elements can be distinguished (Cowan, 1978; Hageman and Roth):

- elements forming a solid-solution with UO_2 show no detectable loss. This is in particular the case of actinides, with the possible exception of Np for which there has been some debate; but Pu for instance appears totally immobile.

- elements with no likely substitution with uranium in the uraninite lattice present variable losses for alkalis, alcaline earths and rare gases (up to 100%) or lower (e.g. 0-20% for zirconium and neodynium).

Moreover, three main mechanisms for the escape of elements from the uraninite lattice have been identified (Cowan, 1978): i. fission recoil, which could have contributed to about 5-10% of the loss of fission products; ii. uraninite dissolution which would be responsible for an estimated 10% of migrated uranium; the possible role of alpha-radiolysis on uraninite dissolution has also been advocated; iii. solid-state diffusion which would have been the major mechanism, in particular for alkalis and rare gases. Quantitative data could even be deduced. For instance, in the case of Cs, Xe, Rb and Kr which are lost, a diffusion coefficient of $4\ 10^{-26}$ m^2/s has been estimated whereas it would have been of only $9\ 10^{-27}$ m^2/s for Mo and Tc which are partially retained. This early work should probably be confirmed by new studies on samples from the reactors discovered recently, notably by means of techniques (e.g. SIMS) which have now better detection limits and precision. Unpublished results obtained recently (Holliger, 1990) show the formation of metallic alloys at grain boundaries, a phenomenon already suggested in early works and also known to occur in spent fuel (Johnson and Shoesmith, 1988). Again, this would demonstrate a good analogy between both materials.

No validation of geochemical models have been performed yet at Oklo.from a point of view which would be useful for studies on the disposal of nuclear wastes.

A number of studies have been dedicated to radiation effects in uraninite. For instance at Oklo, most of them intended to decipher whether the present uraninite had "seen" the nuclear reaction. It has been concluded (Dran et al., 1978) that uraninite exhibits evidences of both in situ recrystallisation (the "normal" uranium ore of this site being pitchblende) and intense bombardment which proves that this mineral was already present during the nuclear reactions. In all experiments so far conducted in the laboratory (e.g. by neutron irradiation or ion implantation), no evidence of uraninite amorphisation has been reported, even for doses of a few dpa. But, in varied natural samples, the formation of alpha-tracks is strongly suggested. The dissolution of these tracks would be responsible for the preferential leaching of daughter actinides (^{234}U, ^{230}Th and ^{228}Th) compared to their parents (^{238}U and ^{232}Th, respectively). Moreover, the self annealing of these tracks has been proven to occur with a mean half-life of about 15,000 years (Stout et al., 1988). Finally, the healing of the global radiation damage in natural uraninites, with temperature and time, occurs in two main stages which have been investigated in detail.

Other phenomena (thermal, mechanical) have not been addressed by means of analogues.

5.3 Ceramics

Since the mineral constituents of the major proposed ceramics have very good natural analogues, the latter have been intensively used for the performance assessment of these waste-forms (see the review of Lutze and Ewing, 1988) . Most work has been done on mineral stability and radiation effects. Indeed, these natural minerals commonly contain high amounts of radiotoxic analogues (U, Th and REE) in concentrations up to a few percent.

Concerning the mechanism and rate of dissolution in the environment, only qualitative information are available but it is known that these minerals (e.g. zirconolite, perovskite, sphene, monazite, etc.) have a long-term durability in a wide variety of geologic sites, up to about 2 billion years. Moreover, in appropriate environments (see below), they can be considered as thermodynamically stable. Numerous laboratory experiments have also been reported (Metson et al., 1983; Boatner and Sales, 1988; Hayward, 1988; Ringwood et al., 1988).

No systematic information exist on the influence of environmental parameters. However, temperature is obviously of great importance. Note that monazite has a prograde solubility, i.e. it decreases when temperature increases contrary to most minerals such as silicates (but alike calcite). The stability of perovskite has also been discussed in detail by Nesbitt et al. (1981) who report that it is stable in conditions of low-silica and high-calcium concentrations but unstable when high-silica and carbone dioxide concentrations are present. It then transforms into calcite and sphene.

Few data are available on the formation of alteration products but, as an example, laboratory experiments on both ceramics and mineral analogues have shown that titanates tend to alter into TiO_2, which forms a protective coating on the surface, thus explaining a steep decreasing of leach rates with time (Ringwood et al., 1988).

The behaviour of elements important for safety (or their chemical analogues) has not been investigated systematically but it is acknowledged that U, Th and REE are strongly retained in the lattices of such minerals and that, in most conditions of interest, their release imply te destruction of the matrix itself.

On the contrary, radiation effects have been extensively studied (Cartz et al., 1981; Dran et al., 1981; Fleet and Henderson, 1986; Greegor et al., 1986), and this is a topic where natural analogues revealed to be particularly useful. One illustration of this statement is that a comparison of minerals naturally metamictised and artificially bombarded by low-energy heavy ions similar to alpha recoils (Headley et al., 1983) have helped demonstrate that ion implantation can be, in appropriate conditions, a good simulation tool for studying radiation effects. Such studies on both types of samples have shown that these minerals exhibit a high resistance to amorphisation, even for very high doses of irradiation (notably linked to alpha decay). The mechanism of amorphisation could be studied in detail; it basically proceeds via the growth and overlapping of amorphous domains, and it is accompanied by an increase in the volume lattice inferior to 3%. Authors have observed a quantitiative retention of uranium, thorium and decay products (except helium) in highly damaged minerals. Moreover, the presence of alpha tracks is strongly suggested by various works (Dran et al., 1981; Eyal, 1983; Eyal and Fleischer, 1985; Eyal et al., 1986) The preferential dissolution of these tracks (by a factor of ten compared to the bulk mineral) is responsible for a preferential leaching of the daughter products ^{234}U, ^{230}Th and ^{228}Th. Finally, an important mechanism of self-annealing of alpha tracks with time has been evidenced. As an example, a mean life time of about 2,000 years has been estimated in the metamict pyrochlore whereas it reaches 100,000,000 years in the crystalline structure (Lumpkin and Ewing, 1989) and 15,000-18,000 years in the crystalline thorianite, uraninite and monazite (Eyal et al., 1986).

Other phenomena (e.g. thermal, mechanical) have not been addressed on natural analogues. In particular, the possibly important effect of self-fracturing of irradiated ceramics (due to anisotropic expansion of the lattice), which has been observed in the laboratory on Pu-doped Synroc (Clinard and Rohr, 1981), has not been studied on natural samples.

5.4 Cement-based materials

Some works have been reported on both old cements, for a maximum period of 150 years, and archaeological binders of ages up to about 2,000 years (Steadman, 1986, Jull and Lees, 1990). The analogy of such binders with modern cement is, in most cases, very poor, but there are some instances where major consituents of modern cement (e.g. calcium hydrosilicates labelled CSH, ettringite, etc.) have been formed, due to specific conditions of cement preparation This in particular the case where binders have been made up of fired clays, volcanic rocks (e.g. pozzolane), etc., which bring both silicon and aluminum to the system. In those cases, silicates, silico-aluminates, and possibly aluminates, could form during the setting of the binders and the analogy between archaeological artifacts and modern cement is then worth the study.

Two investigations can best illustrate the use of natural analogues in this field for assessing alteration processes. The first has been conducted on samples collected from the Hadrian wall, in the north of England (Jull and Lees, 1990), the second in gallo-roman baths from the southwest of France (Rassineux et al., 1989). These studies have confirmed that, on the long-term, the carbonation of hydrosilicates is the main mechanism of alteration of binders. Indeed, whenever CO_2 has access to the material, CSH can rapidly transform into calcite throughout the bulk. This process is enhanced by the presence of fissures.

The evolution of CSH over 1800 years could also be specified. It was commonly thought that such amorphous substances should organise with time and transform into crystalline minerals, such as their natural counterparts (tobermorite, gyrolite, etc.), which are high-temperature alteration products of basic and ultrabasic rocks. From a pure thermodynamic point of view, this is likely expectable but these archaeological analogues show that this transformation does not occur over this time span, probably because of its slow kinetics. Analogues also suggest that the lower the CaO/SiO_2 the higher the stability of the CSH, which exhibits no evidence of crystallisation nor better organisation. Figure 10 shows in Si-Al-Ca triangular diagrams that constituent phases of modern and gallo-roman binders may be analogous.

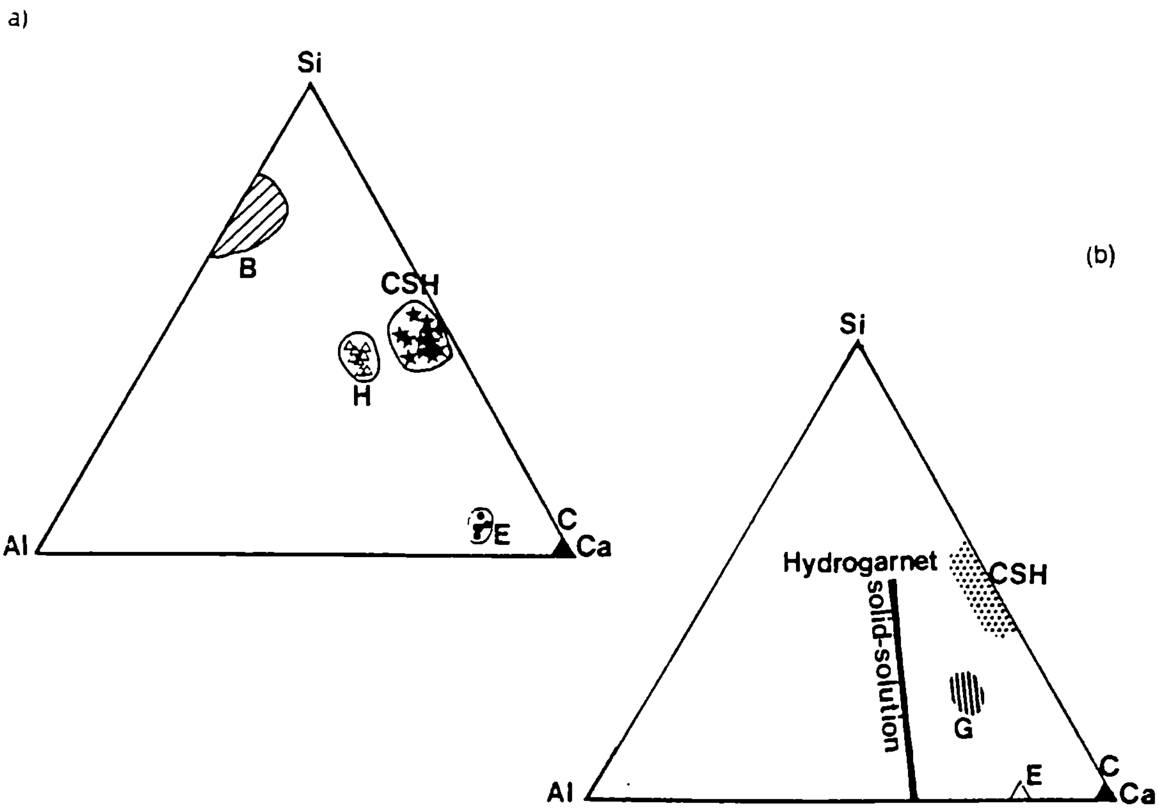

Figure 10: Al-Si-Ca triangular diagrams showing the mineralogical anlogy between constituents of a Gallo-roman binder (a) and a modern pozzolanic cement (b) (from Rassineux et al., 1989).

Other phenomena of interest have not been addressed yet but this is certainly a field to be developed in the future.

5.5 Bitumens

Very few works have been devoted to analogues of bitumens. Only a field study and an excellent review of the Finnish literature are available (Helmuth, 1989a, 1989b), on which this section is based.

Natural bitumens are complex organic matters which are formed during the carbon cycle, the main origin of which is the living organisms. It is a step in a series of geological events, mainly associated to the diagenesis of sediments, which can also lead to the formation of oil, petroleum, asphalt, etc. The average composition of this class of material is the following:

C: 80-88%
H: 8-11%
O: 1-12%
S: 1-7%
N: < 1.5%

Classically, the maturation of natural organic matters in the environment is best represented by their H/C and O/C ratios which lead to define evolutionary paths, according notably to their origin. From a molecular viewpoint, bitumens are constituted of saturated and aromatic hydrocarbons, resins, heterocyclic compounds, high-molecular asphaltenes, carbenes (MW: 300 to >10,000). To show the complexity of such molecules, figure 11 illustrates the assumed detailed structure of asphaltene.

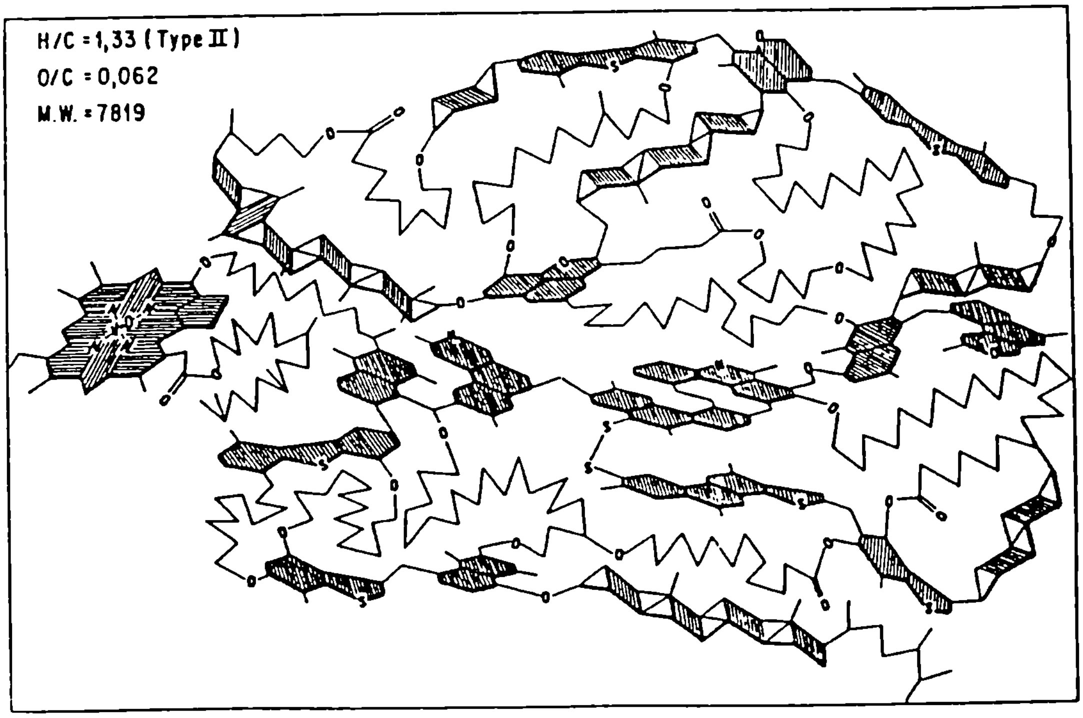

Figure 11: Molecular structure of asphaltene (from Helmuth, 1989b).

One considers that the analogy with technological bitumens, which are indeed a distillation fraction of petroleum, is quite good for both physical and chemical properties. Archaeological artifacts, mainly from the Middle East (Babylonia, Assyria, Sumer), have been made from natural bitumens extracted locally and, apart from their evolution with time, have comparable characteristics. It should also be pinpointed that the definition of bitumen is only based on the behaviour of organic matter during a standardised treatment where properties of solubility, fusibility and their solid/liquid character are considered (figure 12). In effect, bitumen are simply (and arbitrarily) defined as organic matter soluble in carbon disulfide whereas, for instance, petroleum must be in addition liquid and have a low nitrogen content.

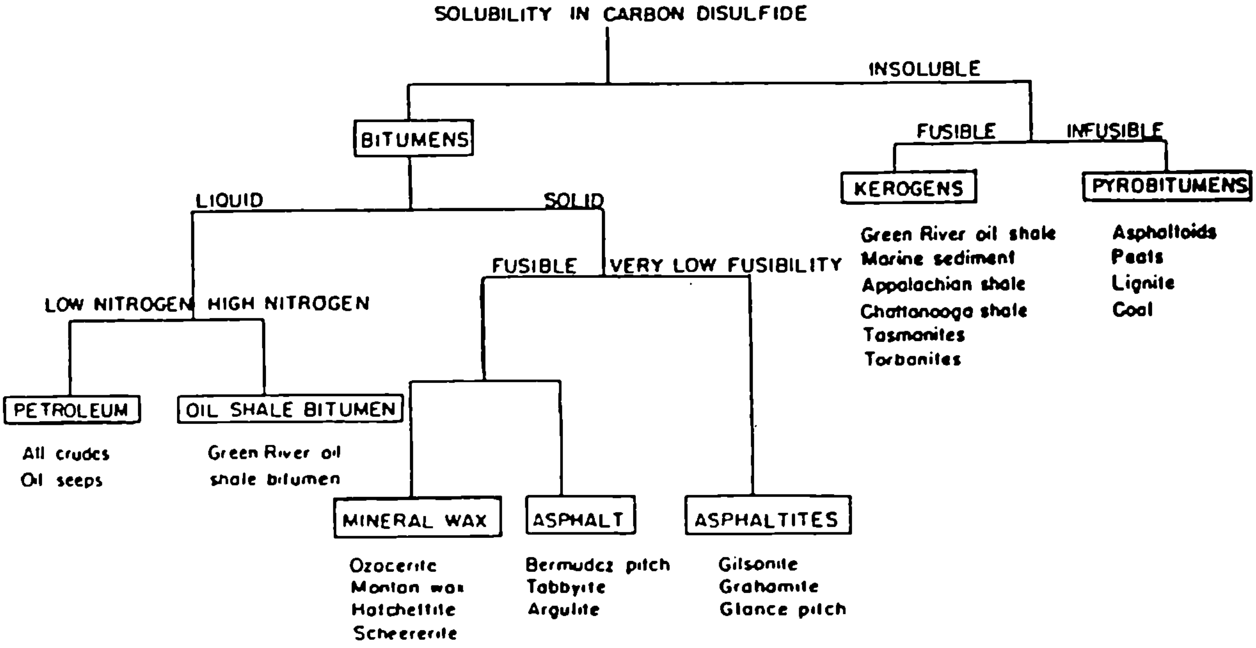

Figure 12: Terminology and classification of some natural organic matters (from Helmuth, 1989b).

Many information are available on the alteration of bitumen which can help develop a tentative conceptual model, inject quantitative data and fix initial and boundary conditions. Concerning the mechanism of alteration, it is known that such materials are intrinsically unstable but the kinetics of their evolution is extremely slow, in particular at low temperature (<100°C) and in the absence of catalysts and living organisms (notably certain bacteria). Since bitumen is used only as a waste-form for low- and intermediate-level waste for shallow-land disposals, such a low temperature can be guaranteed. The occurrence, and activity, of living organisms is, on the contrary, a key issue. In addition, archaeological evidences (> 5,000 years) suggest that bitumens are stable materials, and can preserve their properties of adhesivity and impermeability, over such periods of time, if they do no suffer any major mechanical alteration. The observed evolution is then merely an increase in hardness (defavourable to their mechanical resistance, bitumens becoming brittle) and in the oxygen concentration.

Two main paths of evolution can be defined:

- the **diagenetic alteration**, where temperature is the ruling parameter. In fact, occurrences of bitumens are known in the range 0-4000 m, which corresponds to temperatures up to a few hundred °C. The main observed evolution is here the liberation of light molecules (e.g. saturated hydrocarbons) and the polymerisation of molecules (asphaltenes) leading to the formation of pyrobitumens (see figure 12). Meanwhile, the solubility and the fusibility of the material markedly decrease.

- the **weathering**, where both oxidation and biodegradation are involved. Here, the main evolution is the leaching of light soluble fractions (e.g. paraffines, hydrocarbons) and biodegradation, which appears again to be a major means of bitumen alteration, occurring in conditions of high O_2, high NH_4/PO_4 ratio, low temperature and salt concentration (< 20%) and with no H_2S. The positive role of salts should be stressed in the context of a possible disposal in salt formations. During alteration, the concentrations of N, S and of asphaltenes increase whereas that of N-alkanes markedly decreases. One also observes the evaporation of lighter fractions (but polycyclic terpanes are stable) and oxidation of the material. This evolution path leads to the formation of humic acids, then organic acids and eventually carbon dioxide and water.

Some indications can also be drawn for the behaviour of elements like V, Ni and U. Indeed, it is known that the former two exhibit strong covalent bonding with porphyrin complexes. Such bonds are very stable during the evolution of the corresponding bulk sediments (lithification, diagenesis, migration and entrapment). Moreover, it should be pinpointed that the degradation products of bitumens (e.g. humics with MW > 100000) also present high sorptive properties for V and Ni. A regards uranium, this element can be fixed to bitumen in concentrations up to a few percent. Indeed, it is well known that many uranium ore bodies in sediments are closely associated with organic matters, including bitumens (for instance at Oklo in zones10-13). Two mechanisms are still debated for the fixation of uranium, namely the sorption or ion exchange of the uranyl cation (UO_2) on humics, asphaltenes, etc., and the formation of micro-crystals of uraninite. The latter process can indeed be simulated in the laboratory by heating at a few hundred degrees, during a few minutes or hours, bitumens where uranium is homogeneously dispersed at the atomic scale. The formation of UO_2 (plus other actinides) micro-crystals is hence a likely long-term evolution of bitumens confining alpha-emitters. Some leaching of bitumens is observed at the surface of the earth, but the mobility of uranium upon such a process seems limited to a depth of about 20 m. It is extremely important to consider, in the framework of waste disposal, that the release of metals, as inferred from natural analogues, necessitates the destruction of the bitumen matrix itself.

These high concentrations of uranium also allow to investigate radiation effects. The evolution under alpha bombardment, due to the decay of this element (and of Th), seems to be the polymerisation of the organic matter towards asphaltites and tucholites (material where Th, U, C, H and O are dominant). One thus observes the aromatisation of molecules with a corresponding loss of functional groups and aliphatics. Surprisingly such an evolution is favourable to the increase of the resistance to radiation of the material. Meanwhile the H/C ratio decreases whereas the O/C ratio increases. Finally the preferential release of uranium, upon irradiation of the bitumen, leads to a relative enrichment in thorium and rare earth elements.

5.6 Resins

There is almost no information on the long-term stability of resins in the environment (Helmuth, 1989b). The value of the analogy with natural resins, such as amber-like materials, is even very questionable. Concerning amber, one knows that their evolution, is quite slow and that they exhibit a good resistance to temperature. For instance at 200°C, they can resist a few Ma and at 100°C a period likely > 20 Ma. Again the evolution of ambers stems from changes in functional groups (acids, esthers), but their alteration seems to be limited to the oxidising outermost part of the earth crust.

5.7 Containers

Works done concern only the corrosion of Fe and Cu (with very limited information on Ti).

Concerning iron (Chapman et al., 1984), archaeological artifacts have allowed the evaluation of corrosion rates ranging from 0.1 to 10 µm/yr (exceptionally a lower value of 0.01 µm/yr has been measured). Surprisingly, these rates are consistent in a wide variety of environments (either dry, wet, oxic or anoxic). Authors estimate that such rates would typically correspond to a mean life time of 10,000 years for a 1 cm-thick container, with a possible mechanical failure at about 2,000 years. Unfortunately, the "pitting factor", which is defined as the ratio of the maximum corrosion rate in etch pits to the mean corrosion rate, and which is a very important parameter in metal corrosion, could not be specified. Metallic meteorites, which are mainly Ni-Fe alloys, are not considered as good analogues. Finally, no data are available for native iron although few sites (e.g. the Disko Island, Groenland) could be studied.

The corrosion of copper has been thoroughly investigated through both archaeological and historical artifacts and native copper (Chapman et al., 1984). The former type of samples demonstrates a long-term stability of copper with corrosion rates in the range 0.025-1.3 µm/years, thus confirming known thermodynamic data. Such values would correspond to a durability of 8,000 to 400,000 years for a 1 cm-thick canister in oxidising conditions. The pitting factor could be evaluated to be of about 3, with a maximum measured value of 25. The investigation of one of the cannon of the Kronan, a Swedish warship that sunk in the Baltic sea in 1676 (see figure 14), has given detailed information on the mechanisms of copper corrosion over about 300 years (Smellie, 1989). It has been shown that the very limited alteration was not due to any simple oxidising reaction but to complex redox processes between Cu(s), Fe(II) and organic matter (figure 13)(Hallberg et al., 1987). The main corrosion products have been identified as an oxide and a hydroxicarbonate of copper (cuprite, which is dominant and malachite, respectively). The data suggest long-term durability of such a copper alloy (96.3% Cu), most of the observed copper released being due to the dissolution of CuO slag inclusions present in the bronze matrix. A corrosion rate of 1.5 10^{-2} mm/year, corresponding to a durability greater than 600,000 years for a 1 cm-thick container, and a pitting factor of 5, have been reported. Native copper samples confirm such a long-term stability but over geological time spans. In addition, one observes the formation of an oxide coating as the main alteration product, with a thickness of about 2 mm in 8,000 years, and a pitting factor of 2-6 (Chapman et al., 1984).

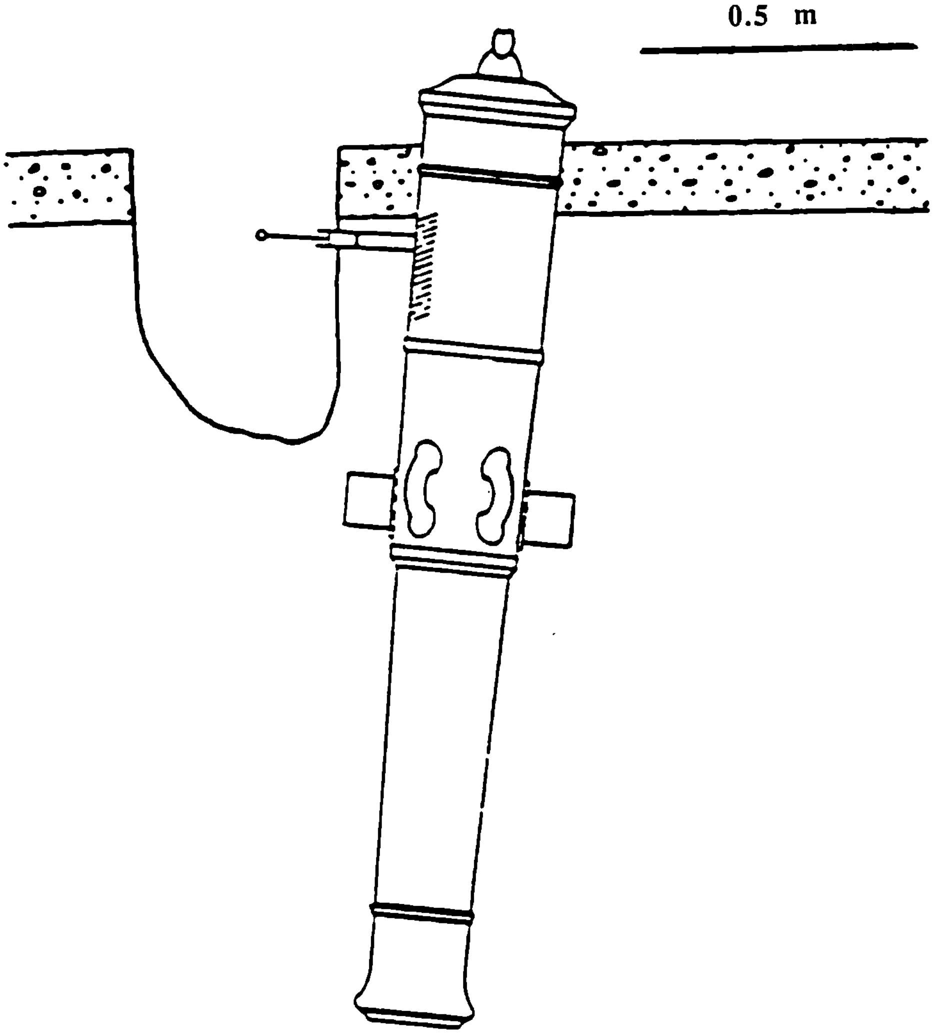

Figure 13: Schematic view of the Kronan cannon partially buried in the clayey sea floor (from Smellie, 1989).

Almost no data are reported on titanium because there do not seem to be any direct analogue. Canadian works dealing with Cigar Lake mention (Cramer, 1989) that the known alteration product of this element, namely TiO_2, exhibits almost no corrosion features over 1,5 10^9 years, in the same geochemical conditions where uraninite has also proved to be stable.

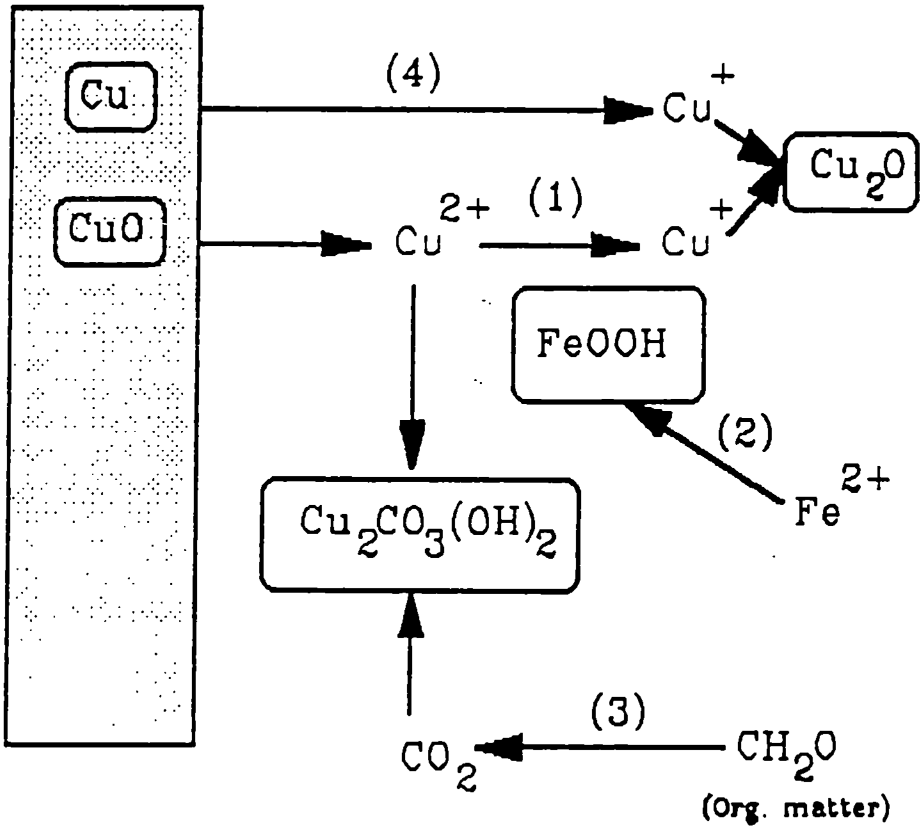

Figure 14: Main processes invoked for the corrosion of the Kronan cannon (from Hallberg et al., 1987).

6. Conclusions

In this paper, we have reviewed the literature on the use of natural analogues for the design and performance assessment of solid radioactive waste-forms. We have shown that, concerning most of the matrices so far proposed or used, quite good analogues are available and that much data (essentially geochemical information) have already been inferred from them. However, up to now, analogues have been essentially used for performance assessment rather than for design of waste-forms, except for some ceramics. Prospects for the future remain nevertheless encouraging. We have illustrated, by a few instances, that both qualitative and, in well defined systems, quantitative data can be inferred from analogues, in particular concerning dissolution and/or alteration phenomena. The a priori use of analogues for designing laboratory experiments could also be useful (e.g. parameters requiring control, key processes to study, methods for accelerated testing, etc., as suggested by Apted, 1990). Extention of such studies to other properties and phenomena of interest to waste disposal (mechanical, thermal, radiative), notably when corresponding to coupled processes, should be favoured in the future.

It has also been stressed that the methodology of study makes a natural material or system be an analogue (and not a list of necessarily arbitrary and changing criteria). Reasoning by analogy is a very powerful heuristic way of thinking but which should be used with caution and carefully mastered. It is nevertheless the only means by which some hints on the very long-term behaviour of waste-forms can be gained.

Finally, the abuse of natural analogues should also be avoided. This includes mislabeling classical geological studies, with the purpose of fund raising, and the use of a wrong methodology. In effect, our starting point should always be the performance assessment of waste-forms, where key issues are to be identified. Only then, the search for an appropriate analogue and its investigation can follow. Finally, the "political" use of analogues, where a global analogy is (too quickly) made with the technological system (which, in such a case, cannot be but a simple metaphor), seems very dangerous.

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NATURAL ANALOGUES FOR THE PREDICTIVE RELIABILITY OF THE ENGINEERED BARRIER SYSTEM FOR HIGH-LEVEL WASTE

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Few things are harder to put up with than the annoyance of a good example.
– Mark Twain

Summary

The engineered barrier system (EBS) is an important subsystem in limiting the release of radionuclides from a geologic repository for disposal of high-level nuclear waste. The purpose of this paper is to identify and discuss the natural analogues to EBS materials (or analogues to their functions) that can be used to confirm their anticipated performance under long-term, repository conditions. Analogues are reviewed relative to material properties of barrier components, radionuclide chemistry within the near-field, and mass-transfer of radionuclides through the EBS. In addition, speculations are offered regarding analogues for future research.

1.0 Introduction

The feasibility of permanent disposal of nuclear waste in repositories located in deep geologic formations is being studied world-wide. The most credible release pathway is interaction between nuclear-waste forms and groundwater, followed by hydrologic or vapor transport to the accessible environment. The primary components of repositories that mitigate release are the near-field and the far-field subsystems. The near-field encompasses the waste package, which is composed of engineered barriers (e.g., man-made materials, such as compacted clay backfill and corrosion-resistant canisters, see Figure 1); the far-field includes the natural barriers (e.g., host rock and hydrologic setting). Taken together, these two subsystems define a series of multiple, redundant barriers that act to assure the safe isolation of nuclear waste.

The far-field has a tremendous capability for the safe isolation of nuclear waste. Considerable international effort has been directed toward finding sites that have "favorable" characteristics (e.g., low groundwater flow, highly sorptive minerals, low redox (Eh) potential, unsaturated hydrology) for geologic disposal.

There are, however, certain advantages in achieving high confidence and reliability in nuclear waste isolation by the engineered barrier system (EBS), schematically shown in Figure 1:

- EBS components can be designed and constructed with well-described, uniform properties; in contrast, the geologic setting can only be partially characterized, with unavoidably large uncertainties because of natural heterogeneities.

- Evaluation of the performance of individual and assembled components of the EBS can be tested readily over a wide range of controlled conditions. In contrast, the performance of the far-field must be based on ambient characteristics of the geologic site. The ability to examine site performance under alternate conditions is extremely limited, both in control of test conditions and in the spatial portion of the host rock that can be tested.

- Components of the EBS can be designed to provide acceptable performance over a wide range of conditions. Acceptable or "favorable" characteristics of a site reflect current conditions. The constancy of these site characteristics over time periods of tens and hundreds of thousands of years is open to question and cannot always be predicted with confidence.

These advantages for the EBS do not obviate the need for performance evaluation of natural barriers. They do, however, dictate a balanced isolation strategy based on both systems.

Predictive reliability is the assurance that the actual performance of a system or component will be as good or better than the predicted performance. A problematical aspect in establishing the predictive reliability of the near-field, as well as the far-field, is time-scale. Engineered barrier materials are assigned functions, based on their properties, that must be maintained over time scales of thousands of years and longer. Such time periods lie well outside the experience for engineering and materials science. Geochemistry and petrology, however, provide a set of well-accepted principles for evaluating materials performance under geologic conditions for thousands of years and longer. Archaeology is also concerned with the long-term durability of man-made materials, albeit over a much more restricted set of time scales and conditions at the earth's surface. Judiciously selected "natural analogue" or "human analogue" studies from these respective research fields can, therefore, provide an extended time scale over which the predictive reliability of engineered barrier materials can be confirmed.

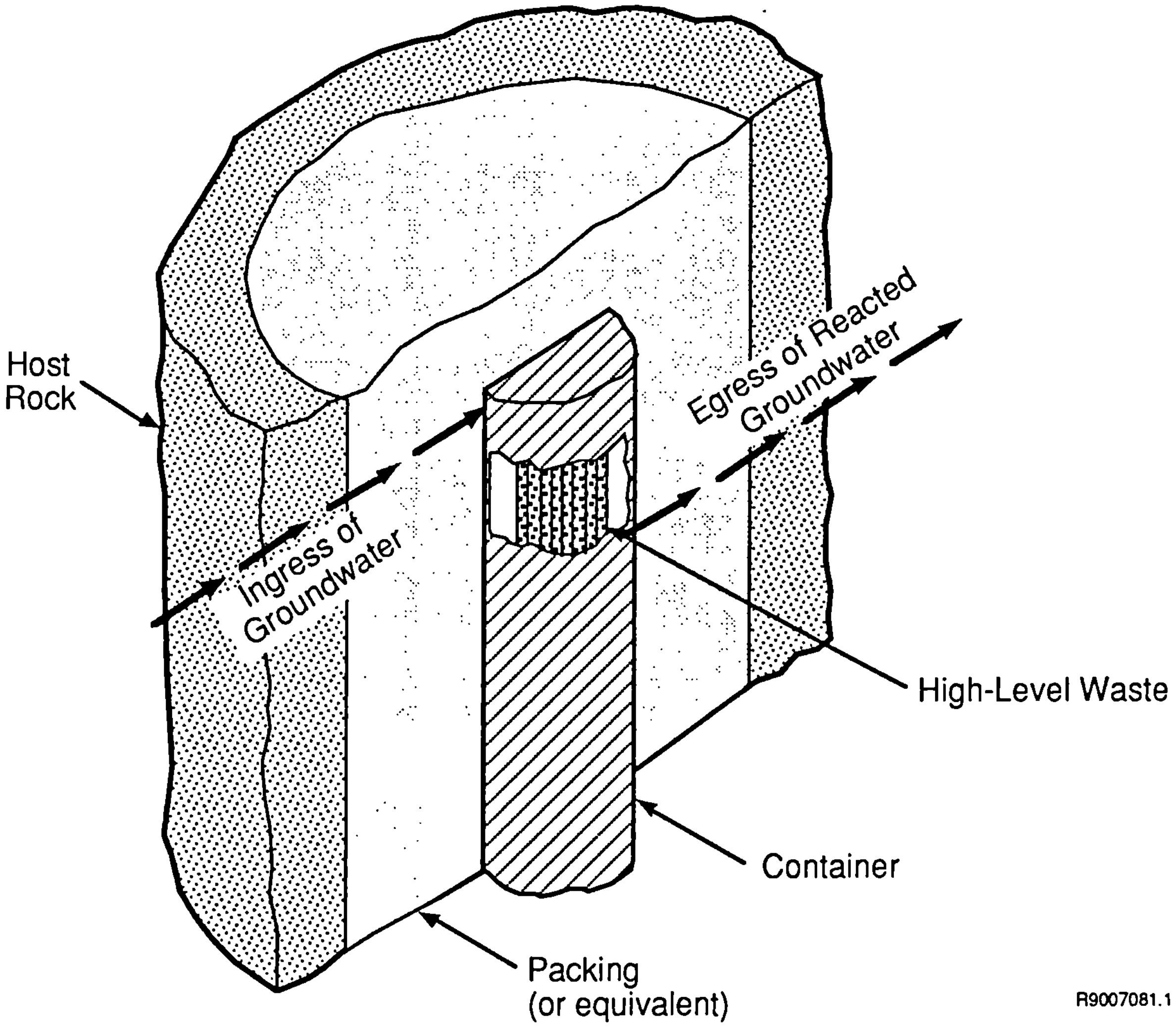

Figure 1. Schematic Diagram of Engineered Barrier System (EBS) for High-Level Nuclear Waste Packages.

The purpose of this paper is to review recent studies of natural analogues, as well as certain human analogues, as they relate to the EBS of a high-level nuclear waste repository. Emphasis is placed on selected studies of analogues that are well-founded and speculations that may prove to be useful. Interested readers are urged to pursue the cited references for more details.

2.0 Application of Analogues

McKinley (1989a; 1989b) has cogently reviewed the application of natural analogues to performance assessment. A key point made by McKinley is that, "[T]he essence of the natural analogue is the aspect of testing models - whether conceptual or mathematical - and not a particular attribute of the system itself." Natural analogues need not match repository-specific conditions to be useful in validating predictive assessment models. Predictive models for the EBS are predicated on the design function of the individual barriers and their expected behavior under geologic conditions. Natural and human analogues applied to engineered materials have largely focused on validation of these models (or their predictions), and are reviewed in subsequent sections.

The associated use of natural analogues to guide experimental work is, however, often overlooked. Specifically, studies of active geothermal systems (Browne 1978, Giggenbach, 1984) and low-grade metamorphism (Zen and Thompson 1974) can provide important insights on how physicochemical parameters control the direction and rate of processes in the near-field. Grandstaff et al. (1990) have demonstrated the consistency between short-term laboratory tests and long-term geothermal systems in predicting the composition of near-field fluids. The relative effects of temperature, pressure, flow rate (permeability), fluid composition (e.g., Eh, pH, dissolved volatiles), material composition, and duration can be systematically correlated from natural analogues to design programs for data collection. Indeed, attempts to "accelerate" short-term (months to years) laboratory tests to provide data representative of much longer durations should be based on these correlations developed from natural systems (Apted et al. 1987).

Furthermore, natural analogues could be used to evaluate the adequacy of current test apparatuses. Evidence from active geothermal sites clearly demonstrate the importance of H_2O and CO_2 as reactive components of the fluid phase, the consequence of boiling (i.e., formation of a two-phase system and partitioning of volatiles), the effect of temperature or pressure quenches, and the significance of open- versus closed-system conditions on geochemical reactions between solid and aqueous phases. Unfortunately, many of the present apparatuses for barrier material testing fail to realistically incorporate one or more of these factors in their design.

3.0 Natural Analogues of Barrier Materials

An EBS is designed to 1) contain radionuclides for an initial period following emplacement of nuclear-waste forms in a repository (Containment Period), and 2) assure acceptably low release rates of radionuclides to the far-field following the loss of containment (Controlled-Release Period). The Containment Period is met by encapsulating the waste form in a metal or ceramic canister (container). A surrounding layer of backfill (also called buffer or packing) material may be included in EBS designs. This has the primary performance function to prevent ground water flow through the emplacement hole and secondary function to condition the composition of the water that re-saturates the backfill. Even with good engineering control, however, total containment will eventually fail and ground water will eventually contact the waste form. The Controlled-Release Period is achieved by either 1) limited access of water at "dry" sites (e.g., salt formations, sites located above the water table) or 2) diffusion-limited mass transfer of nuclides through a surrounding layer of low-permeability clay backfill at hydrologically saturated sites.

The temporal P-T histories of the EBS in hydrologically saturated and unsaturated (i.e., above the water table) sites are shown in Figure 2. The P-T trajectory of a typical (30°C/ km) geothermal gradient is also included for comparison. For the EBS at both sites, the initial, post-emplacement pressure is equal to the atmospheric pressure of 0.1 Megapascal (1 bar). Emplacement of high-level radioactive waste locally increases the temperature to >100°C, and

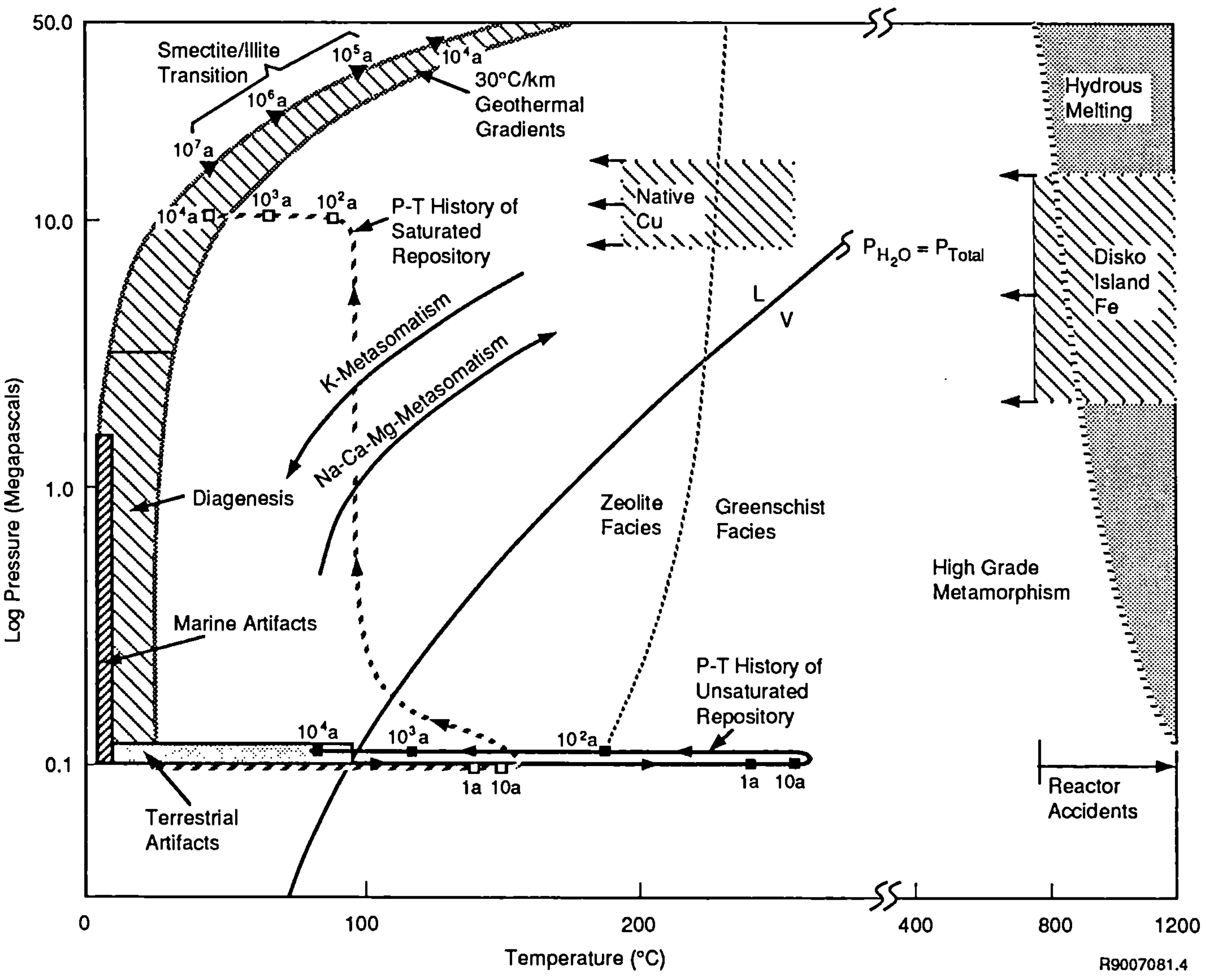

Figure 2. Pressure-Temperature (P-T) Diagram Showing Conditions within the EBS over Time, and the Range of P-T Conditions for Certain Natural- and Human-Analogues Described in the Text.

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any co-existing water will boil at the two-phase univariant curve. Assuming ventilation or open-system transport, vapor-only conditions will be reached within the EBS, as well as a portion of the surrounding rock.

At this point, the P-T trajectories of the two sites begin to diverge. For a hydrologically saturated site, the partial pressure of water will increase until the liquid-vapor curve is encountered and fully saturated conditions under elevated pressure and temperature will be obtained. The timing for this process depends on a number of factors, including heat-generation rate and permeability of the surrounding host rock (Pruess and Bodvarsson 1982). For the unsaturated site, the pressure remains at about 0.1 Megapascal; the decreasing heat-generation rate causes a gradual decrease in temperature until the liquid-vapor curve is encountered at approximately 100°C. There are two important consequences of this long-term boiling. The first is that aqueous transport of radionuclides is effectively eliminated during this initial period. Second, the chemical composition of the water that does eventually enter the EBS may be significantly altered from the ambient composition. For example, the consequent loss of dissolved CO_2 will raise the pH, with a concomitant increase in K+/H+ ratio (Criscenti and Arthur 1990).

3.1 Containers/ Overpacks

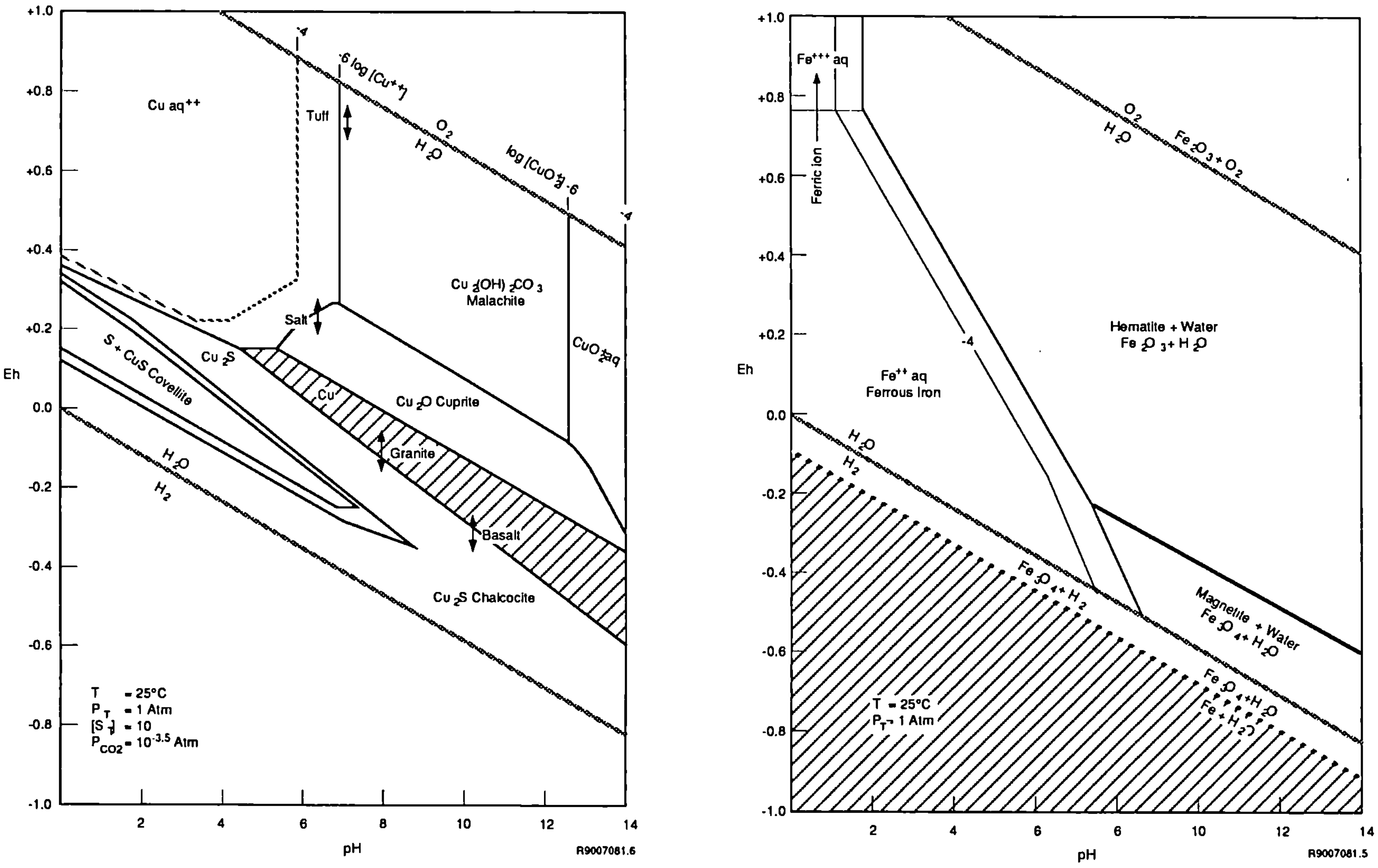
The function of the container/ overpack is to isolate the waste from ground water for a designated period of time. Containment strategies range from long-term containment (> 10^5 years), assuring the elimination of most radionuclides by radioactive decay, to relatively short-term containment (up to 1000 years), isolating waste from ground water until after the thermal pulse arising from short-lived fission products. There are three types of containers: 1) stable materials under expected repository conditions, for which the mass-transfer rate of reactants (or products) rather than interface kinetics can be used to establish extremely low corrosion rates, 2) corrosion-resistant materials that have an extremely low general-corrosion rate because of the formation of passive/ insoluble surface layers, and 3) corrosion-allowance materials that have a moderate general-corrosion rate but are inexpensive enough to fabricate into relatively thick-walled containers.

3.1.1 Stable Materials

In neutral to alkaline repository ground waters under mildly reducing conditions, copper is calculated to be thermodynamically stable (Figure 3a, from Garrels and Christ, 1965). The lower (reducing) limit for this field of stability is determined by the reaction of metallic copper with dissolved-sulfur species to produce chalcocite (Cu_2S), and is a function of the activity of sulfur species as well as Eh and pH. The upper (oxidizing) limit for copper stability is set by oxidation to cuprite (Cu_2O), and depends on Eh and pH only. Coupled with diffusional mass-transport constraints on the supply of oxidants imposed by a clay backfill, this predicted stability has been used to establish a lifetime of 10^5 to 10^6 years for thick-walled copper containers (KBS 1983). Both copper stability and the mass-transport constraints can be validated by natural analogues.

Copper is one of the few elements, and certainly the least expensive, that occurs in its native state under geological conditions relevant to repository isolation. The most prominent natural analogue is the massive native-copper deposits on the Keweenaw Peninsula, Michigan, U.S.A. (Crisman and Jacobs 1982). These deposits occur in the Precambrian (~500 million years old) Portage Lake Volcanics, a series of basaltic lava flows interbedded with conglomerates (Figure 2). Some copper occurs as veins cutting these rocks, but principally either in the lava flows filling amygdules, or in the conglomerates filling interstices. The copper was initially distributed as a trace component in silicate minerals of underlying formations; later, hydrothermal waters caused propylitic alteration (zeolite facies) of the rocks, mobilized the copper under acidic conditions, and deposited it as metallic copper upon contact with the reducing, sulfur-poor basaltic lavas and conglomerate beds. *In situ* occurrences show negligible signs of post-emplacement alteration or mobilization.

This natural analogue for copper can be inverted. Massive metallic copper does not occur as a primary phase in fresh basalt, even under reducing conditions at which it is calculated to be stable. Instead it occurs initially as a trace component in silicate and sulfide phases. This is a



[a]

[b]

Figure 3. Diagram of Eh-pH Stability Fileds for Phases in the Cu-H2O-O2-S-CO2 System [a] and the Fe-H2O-O2 System [b] (adapted from Garrels and Christ 1965). Stability fields for metallic copper and iron are shown in diagonal shading.

consequence of copper's low abundance and the tendency toward free-energy minimization (via formation of solid solutions) within natural systems. Formation of massive metallic copper nodules and veins results from release and migration under low-grade propylitic alteration of the host basalt. Viewed in this way, the same Keweenaw deposits support the contention that copper can be extremely reactive and mobile under certain geological conditions (Jacobs 1984). The utility of such an analogue, therefore, is not the 500 million year persistence of metallic copper, *per se*. Rather, it validates that the reactivity and mobility of copper in natural systems (and by analogy, repository systems) can be predicted using geochemical principles and thermodynamic data.

Copper artifacts have also received study as analogues (Johnson and Frances 1980), although few of them have compositions similar to the relatively pure copper considered as a container material. In most cases these artifacts can be dated accurately, which is an advantage. A disadvantage is that constancy over time of the environment can not always be established. Furthermore, the selected artifacts may be biased because objects of similar age, but with higher corrosion rates, might have been completely corroded. Nonetheless, existing copper artifacts support an upper-bound, long-term corrosion rate of approximately $5x10^{-4}$ mm/ year (Johnson and Frances 1980). Long-term corrosion rates from natural analogues, however, are relatively unimportant for copper. This is because the corrosion rate of copper containers emplaced in clay backfill will be controlled by diffusional transport rather than interface kinetics.

One of the better archeological analogues for the corrosion behavior of copper is a study of a bronze cannon (Hallberg et al. 1988). The cannon has been buried in clay sediments in the Baltic Sea for over 300 years. Thus, the initial composition of the cannon, duration, temperature, and solution composition are well-known for this analogue experiment. Results show that cuprite and malachite are the principal corrosion products, derived from selective oxidation of the tenorite inclusions within the bronze alloy. The Cu-rich (96.3% Cu) bronze matrix shows little corrosion, estimated to be less than 10^{-4} mm/ year. Because the cannon is surrounded by clay (largely illite and montmorillonite, partly as mixed-layer clay minerals), the potential exists for extending this analogue to evaluate mass-transport models for near-field release (see Section 4.2).

3.1.2 Corrosion-Resistant/ Corrosion-Allowance Materials

For corrosion-resistant and corrosion-allowance materials, one of three basic failure modes will determine the time to loss of containment: 1) localized corrosion of the bulk container,
2) uniform corrosion until the container thickness has been reduced to a yield threshold,
3) preferential corrosion at the welds. Corrosion-resistant materials are usually assumed to fail by the first mode and corrosion-allowance materials are assumed to fail by the second mode; it is arguable, however, that both materials are more likely to fail by the third mode at the heat-affected zone of weldments.

There are rare occurrences of metallic iron in nature. This scarcity is attributable to the instability of metallic iron with respect to pure water under expected repository conditions (Figure 3b); pressures for hydrogen gas necessary to achieve an equilibrium between water and metallic iron are several times greater than the lithostatic pressure for a repository located 1 km below the surface (Neretnieks 1985). Iron meteorites are composed largely of α-Fe, kamacite, containing approximately 7% Ni, and nickel-iron, taenite, containing 30 to 75% Ni. These phases are compositionally dissimilar to the mild steels or stainless steels proposed for container materials. The oxide coatings (rinds) on meteorites and stainless steels both form a spinel phase, although there is a complete absence of Cr in spinels associated with iron meteorites. Whether the mere structural similarity of spinels can be used as an analogue for long-term performance of stainless steels is questionable. Stainless steels are expect to fail by localized corrosion, which is strongly dependent on the Cr-content of the surfacial spinel phase, stress conditions, and formation of chemical micro-environments. None of these factors are operative under the conditions in which meteorites are formed or found. Study of rinds from iron meteo-rites would, at best, provide analogue data on a corrosion process that is largely irrelevant.

Terrestrial iron does occur as a secondary product formed from reduction of iron phases by assimilation of carbonaceous material (Bird et al. 1981). Disko Island, Greenland is the most prominent locality, where alpha-iron (ferrite) and iron carbide (cohenite, Fe_3C) fragments, ranging from small grains to large blocks, are found in basalt that has intruded carbonaceous sediments (Bird et al. 1981). Cohenite is the Ni-bearing form of the pure Fe_3C phase that occurs in steels, cementite. Pearlitic textures (intermixture of ferrite and cohenite) surrounding large crystals of ferrite are present in Disko Island basalts (Lovering 1964). This is similar to the texture found in cast steels being considered as container materials. The iron at Disko Island is the result of a high temperature, non-aqueous event and has little relevance to container studies (Figure 2). Analysis of the subsequent reactions in this system could, however, provide insights to the long-term behavior of iron under repository conditions. Reported alteration reactions encompass both oxidation (i.e., production of wustite and magnetite from ferrite) and hydration (i.e., production of hisingeritic clays) around metallic spherules (Bird and Weathers 1977). Further study of subsequent alteration reactions at this locality may be valuable.

The main analogues for these materials are derived from archaeological studies of ancient metals. Unfortunately, this immediately eliminates their direct application to advanced corrosion-resistant materials, such as stainless steels and titanium, which are most likely to fail by the first mode. Furthermore, there are no archaeological samples representative of the welding effects that will be occur during sealing of containers. Analogues appropriate for the third failure mode are, therefore, also eliminated. Only uniform corrosion of mild steel, arguably a mechanism unlikely to control container failure in the long-term, is suitable for study by archaeological analogues. Furthermore, the abundant impurities in ancient wrought-iron compared to modern steel makes their connection all the more tenuous.

The interpretation of iron artifacts are subject to all of the advantages and disadvantages outlined for copper artifacts. Studies of selected iron artifacts have been reviewed (Johnson and Frances 1980), although recent British excavations of wetlands in which iron (and bronze) artifacts were ritually disposed 3000 years ago may contribute new data (Keys 1990). Inferred corrosion rates of iron artifacts vary over roughly five orders of magnitude, attributable to a range in depositional environments from arid conditions to sea water. If extreme values are discarded, corrosion rates for iron artifacts cluster around a value of $\sim 10^{-3}$ mm/ year (Johnson and Frances 1980). It is clear that careful measurement of the composition of co-existing water with iron artifacts would be prudent if continued study of such analogues are to be useful.

Microbially mediated corrosion of iron-based materials has also received limited attention (Barker 1984; Marsh et al 1986; Grogan 1987). Sulfate-reducing bacteria are of particular concern for the anticipated reducing conditions of repositories. The tolerance of such bacteria for extremes in temperature, salinity, pH, Eh, radiation, and pressure could be established through natural (and human) analogues (e.g., Bath et al. 1987), although nutrient and energy availability could be the actual limiting factors in their viability (West et al. 1986). Biocide/ biostat effects of copper on microorganisms should also be studied.

3.2 Backfill

The design functions of the backfill surrounding the waste container are to:

- provide a diffusional-transport barrier between the waste form and host rock,
- reduce possible tectonic shearing forces on containers,
- prevent the container from settling within the emplacement hole/ tunnel,
- conduct heat from the engineered barriers (i.e., keep near-field temperatures low),
- filter fine particles and colloids that may form during waste package reactions,
- retard the diffusional-transport rate of many dissolved radionuclides.

The first five of these functions are achieved by physical properties of the backfill; hydraulic conductivity, plasticity, bearing capacity, thermal conductivity, and pore size/ tortuosity. The retardation function results from chemical processes, either cation-exchange capacity or sorption capability. Swelling smectitic clays, notably sodium- and calcium-montmorillonite, display favorable characteristics for all of these properties. Because these clays swell upon contact with water, compacted blocks of montmorillonite have extremely low hydraulic conductivities and are effective barriers to advective flow. In addition, swelling of the clay acts to self-heal gaps and to penetrate small fissures in the adjoining rock.

The principal process leading to loss of function for smectites is mineralogic alteration. A distinction must be made between two limiting types of alteration (Giggenbach 1984). At very low fluid/rock ratios, the alteration process is limited to isochemical recrystallization (metamorphism). With increasing fluid/ rock ratios (i.e., increasing flow rates), alteration occurs by one of three metasomatic processes; hydrogen- metasomatism, potassium-metasomatism in major upflow areas leading to potassic and phyllic alteration, and sodium-, magnesium-, calcium-metasomatism with descending and heating solutions leading to propylitic alteration.

The most attention has been paid to the potassium-metasomatic alteration of smectite (S)-to-illite (I). This transformation occurs under the appropriate temperatures and pressures in the subsurface environment with accompanying changes in density, permeability and chemistry (Ahn and Peacor 1986). In sedimentary formations, the relatively slow transition occurs over a range in temperatures from about 55°C to 120°C at a depth of about 2,000 m to 4,000 m (Lahann 1980). A study of illitization from contact metamorphism indicates transformation to 40% illite over a period of 3.4 million years at temperatures ranging from 240° to 105°C (Kamei et al. 1990). For temperatures below 100°C, a rate of 0.3% alteration per million years is estimated (Chapman et al. 1984). One reason for the sluggishness of this transformation is that many phyllosilicates are structurally similar, with corresponding small differences in entropy. Consequently, rates of reactions among these phases have small temperature dependence. Large thermal overstepping of equilibrium conditions is required, therefore, to significantly accelerate reactions.

The smectite-to-illite transition requires the addition of K^+, and to a lesser extent, Al^{3+} (Boles and Franks 1979), either from interstitial water or from available exchange positions in the smectite. Inter-layer water is expelled during the transition and the phase becomes less ordered and less dense. Silica that is released by exchange for aluminum (beidellitization) may be precipitated on the clay or in pores, leading to cementation and loss of plasticity. Authigenic illite has fewer dislocations/grain boundaries and individual grains may be significantly less permeable than smectite (Freed and Peacor 1989). Bulk permeability, however, may be higher for the original compacted bentonite mass. The transition passes through an intermediate stage of mixed-mosaic I/S, i.e., mixed packets of discreet illite and smectite tens of layers thick that are intimately mixed but not inter-layered. The final end-member product is a mixed-mosaic I/S of no more than 80% illite. There is evidence that the transition will not occur if illite is not present in significant quantities, perhaps as high as 20% (Hower et al. 1976). It should be cautioned that previous studies of the smectite-to-illite transition have only investigated natural formations in which smectite was one of several components, and have not involved pure nor compacted material.

The natural analogue studies cited above indicate the dependance of the smectite-to-illite transition on temperature, starting materials, access of water, and duration. At temperatures below 90°C, smectite that is essentially free of initial illite is expected to remain unaltered for more than 10^6 years (Figure 2). Furthermore, if illitization were to occur, the resulting backfill will still be extremely non-conductive and its effective diffusion coefficient may not change significantly (Pusch and Karnland 1989; Pusch 1989). Indeed, a recent study that examined the properties of natural clays, similar in composition to possible alteration assemblages of smectite, show that acceptable performance with respect to physical properties could still be expected (Pusch et al. 1989).

The retardation properties of illite, however, may be dramatically different than the starting smectite. As a caution, it should be noted that the effectiveness of sorption in limiting radionuclide release to the far-field is somewhat over-emphasized, unless backfill thickness is on th the order of one meter or more. Sorption on backfill will reduce or eliminate the release of relatively short-lived nuclides (e.g., Sr-90, Cs-137), but these nuclides are of little consequence if travel times in the far-field are hundreds of years or more. Conversely, sorption by backfill can maintain high, initial-dissolution rates for waste forms and promote higher peak releases of longer-lived nuclides that are of concern to repository safety assessments. Steady-state releases of long-lived nuclides are controlled by the porosity of the backfill, not by sorption properties or even hydraulic conductivity. Illitization would result in only negligible change to the initial porosity of compacted smectite clay and should, therefore, have a negligible effect on long-term releases. It should be noted, however, that relatively thick backfill layers (≥ one meter) effectively delay the attainment of steady-state releases for sorping radionuclides to time scales of greater than 10^7 years (Nagra 1985).

Aside from metasomatic reaction of smectite, metamorphic alteration of sodium-smectite to more stable sodic phases is also possible. Thermochemical calculations predict that albite or paragonite will be the more stable than sodium-smectite (Giggenbach 1984) and hydrothermal tests on bentonite show incipient formation of secondary albite (Allen et al. 1984).

One important issue yet to be addressed by analogue studies is the synergistic reactions between container materials and clay. Specifically, copper derived from the dissolution/ corrosion of the container might participate in an exchange reaction with smectite clays (Pusch et al. 1989). These Cu-rich clays could display different chemical and physical properties than their Na- and Ca-counterparts. Analogue studies of synergistic reaction between iron and clay might also be considered. Iron-rich saponite clay can form in the zone between Na-bentonite and mild steel under simulated repository conditions (Anatatmula and Fish 1987). The properties of this material and the extent of its formation could alter the local characteristics of the backfill. Given the key role of high pressure on iron-clay-water reactions in deep repositories (Neretnieks 1985), it is doubtful, however, that near-surface iron artifacts would represent a realistic analogue. The long-term chemical compatibility between salt and silicates, especially clays, might also be investigated as natural analogues of salt formations as repository sites.

3.3 Waste Forms

Natural analogue studies on the dissolution behavior of waste forms are addressed in a parallel paper for this Workshop (Petit, this volume). Primary release of radionuclides occurs by stoichiometric dissolution of the waste matrix, accompanied by precipitation of secondary mineral phases. The phases that occur and their long-term stability affect the long-term performance of waste forms (Grambow 1984). If a theory can be developed to determine what phases will form and factors that affect their formation, natural analogues can be used to validate these predictions.

Glass is intrinsically unstable with respect to an assemblage of crystalline phases. Thermodynamic and kinetic models for describing such irreversible reactions under aqueous conditions have been formulated (Aagaard and Helgeson 1982; Dibble and Tiller 1981a). Interestingly, field studies show that the alteration of natural glass does not lead to the formation of the most stable phase; rather, a sequence of metastable assemblages are formed during a series of reactions. This well-documented observation is called the Ostwald step rule or law of stages (Fyfe et al. 1958). This phenomenon occurs because the net dissolution rate of glass is high relative to the net growth rate of alteration products, resulting in supersaturation of the coexisting solution with respect to many secondary phases. Apparently, the formation and persistence of metastable assemblages is favored because the nucleation and growth of less-stable phases (e.g., gels, clays, disordered zeolites) lowers the total free energy of the glass-bearing system faster than the nucleation and growth of the more-stable phases (e.g., feldspars, quartz, micas). The most stable assemblage eventually forms only after a series of reaction steps. The duration of these steps, and the effect of temperature, pressure, flow rate, and bulk composition, can be established through study of natural systems, combined with laboratory data on dissolution/ precipitation kinetics.

For example, the paragenesis of authigenic minerals from silica-rich glass in tuffaceous sediments has been studied by Dibble and Tiller (1981b), based on numerous field studies (e.g., Sheppard and Gude 1973; Surdam and Parker 1972; Hay and Sheppard 1977). Figure 4 is from Dibble and Tiller (1981b) and quantitatively shows a step-wise reaction curve versus time. The duration of each step will depend on reaction conditions. Increasing pH and salinity of pore water may lead to higher dissolution and growth rates, compressing the time scale. Likewise, increasing temperature will increase the reaction rates, reducing the time necessary to transform from metastable to most stable alteration phases. Field studies (Keith et al. 1978; Browne 1978) of natural obsidian at Yellowstone, Wyoming, U.S.A. indicate that decreasing permeability (i.e., flow rate) can lead to an extension of the time scale; obsidian is completely altered in one well at 85°C, but persists to 170°C in another, less permeable part of the same formation. In a similar manner, the previously mentioned impermeability of a smectite backfill should inhibit its potential metasomatic alteration to illite by limiting the rate of access of K+. Indeed, the assumption of local equilibrium leading to isochemical metamorphic alteration has been repeatedly validated (Aagaard and Helgeson, 1980).

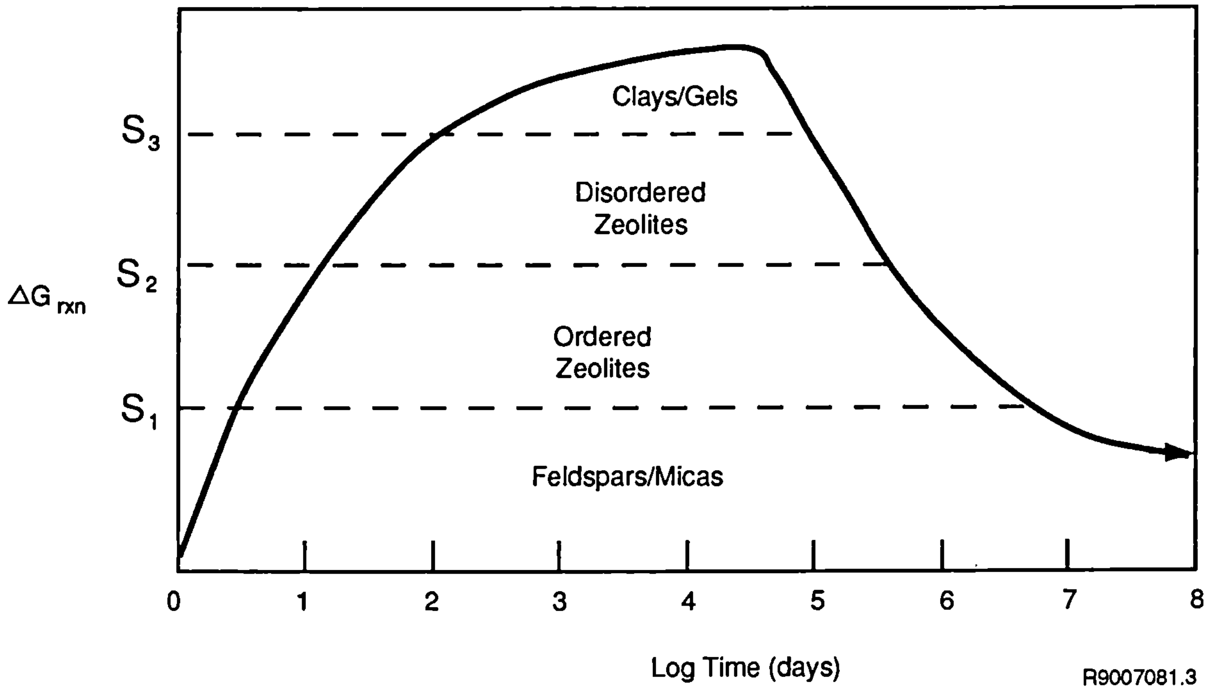


Figure 4. Absolute Value of the Departure from Equilibrium (ΔGrxn) versus Time of Reaction Forming Successively More Stable Phases in Metamorphic Alteration of Glassy Tuffaceous Rocks (adapted from Dibble and Tiller 1981b).

4.0 Natural Analogues of Radionuclide Chemistry and Transport

Mass-transfer theory is well-established and highly refined in the field of chemical engineering, and has proven to be a successful approach to establishing the predictive reliability of the EBS (KBS 1983; NAS 1983; Nagra 1985). It represents a general, mechanistic approach to predict the near-field release of radionuclides, as affected by diffusion, convection, reaction rate of the waste form, solubility, adsorption, radioactive decay, EBS geometry, and other relevant factors. Mass-transfer models place no reliance on adjustable coefficients or arbitrary variables based on empirical fits to laboratory or field data, as do other proposed release models. The mechanistic basis and exact formulation of mass-transfer models permits a high degree of validation to be achieved, thereby providing confidence in extrapolated results. Natural analogues for radionuclide chemistry and mass-transport within the near-field are discussed in the following sections.

4.1 Radionuclide Chemistry

Upon breaching of the container, two chemical processes may affect the release of radionuclides from the EBS to the far-field. The first process is the dissolution rate of the waste form with ground water. Analogues for this process are reviewed in a companion paper (Petit, this Volume). The second process is the establishment of solubility-limits to the concentration of radionuclides at (or near) the waste-form surface. There is a consensus that solubility limits, not dissolution rate, will control the release of most radionuclides from the EBS over long (>100 years) time periods of safety concern (KBS 1983; NAS 1983; Nagra 1985; Pigford and Chambre' 1987).

Numerous natural-analogue studies demonstrate the solubility control of concentration of many dissolved species that can be predicted on the basis of equilibrium thermodynamics (e.g., Giggenbach 1984; Jenne and Krupka 1985; Grandstaff et al. 1990; Henley et al. 1984). Similar studies of low-temperature (<150°C) natural waters also show that some species controlled by electron-transfer reactions (e.g., HS^-/ SO_4^{2-}) may remain in disequilibrium with respect to the redox conditions of the system unless catalyzed by mineral surfaces or microbes (Ohmoto and Lasaga 1982; Lindberg and Runnells 1984). In general, however, studies of geothermal systems support the assumption of local thermodynamic equilibrium, in conjunction with kinetic models derived from transition-state theory, to reliably predict the chemistry of repository ground waters.

Solubility-limits to radionuclide concentrations should be recognized as occurring in the near-field rather than the far-field. The highest concentration of radionuclides in solution is expected to be at the waste-form surface. Mass-transfer analyses indicate that because diffusional transport is much less rapid than expected dissolution rates of waste forms, the concentrations of radionuclides will tend to increase at the waste-form surface until a solubility limit is reached (Pigford and Chambre' 1988). Unless there are tremendous gradients in physico-chemical parameters such as temperature or redox potential (Neretnieks 1984; Garisto and Garisto 1986), it is essentially impossible for radionuclide concentrations in the far-field to exceed the solubility-limits.

Model predictions of speciation and solubility of radionuclides are testable, in principle, by natural analogues. There are factors that make this comparison difficult in practice. These factors include the meager amount of reliable thermodynamic data, the lack of stable elements that are appropriate analogues, and the trace abundances of radioelements.

4.1.1 Thermodynamic Data

The first difficulty has nothing to do with natural analogues, but in making predictions of phases that impose solubility limits in natural systems. It has been pointed out (Bruton 1988) that solid precipitates that sequester radionuclides in the modelling simulations of geochemical reactions tend to be oxides or hydroxides, and less frequently carbonates or phosphates. The dominance of radionuclide-bearing oxides/ hydroxides as predicted secondary precipitates is an artifact of their relatively complete representation in the thermodynamic data base relative to the sparse data set for other radionuclide-bearing solids. Thermochemical data on radionuclide-bearing alumino-silicate minerals, that are the most likely phases to form under repository conditions, are generally lacking.

For example, radionuclide release calculations have been made (Bruton 1988) in which soluble cesium salts are included in the data base but the relatively insoluble cesium alumino-silicate (pollucite) is not. The predicted results fail to show limits to Cs concentration, despite the fact that pollucite is observed to precipitate during short-term waste-form experiments. Predictions of radionuclide chemistry based on conventional "wisdom" from simple systems (e.g., high solubility of cesium) are generally inadequate and should be validated by laboratory or field studies.

Most solubility data on radioelements are collected at standard temperature (25°C) and pressure (1 bar). Heat capacity data for extrapolating results from ambient conditions to higher temperatures are difficult to collect and typically lacking. The radiogenic heat from emplaced nuclear waste, however, leads to elevated temperatures in the near-field. The general absence of these temperature corrections is one of the reasons that solubility constraints are often incorrectly accredited to the far-field rather than to the near-field.

4.1.2 Stable and Radioactive Element Analogues

A limited number of radionuclides have stable isotopes that occur in the natural environment. For other, multi-valent radionuclides, such as Tc and Pu, it is problematical to establish a strict chemical analogy with alternate elements. Studies of ancient natural "reactors", such as Oklo, Nigeria, (e.g., Curtis and Gancarz 1983) and the cycling of radionuclides from testing of nuclear weapons (e.g., Salter et al. 1983) can provide insights to the environmental chemistry of such nuclides. Also, trace amounts of Tc-99 and Pu-239 are formed in nature through nuclear processes. Natural analogue studies of such isotopes from the Koongarra uranium deposit, Australia suggest that uranium minerals effectively retain Tc-99 and Pu-239 on a time scale of 10^6 years (Curtis et al. 1987). It is debatable, however, if standard chemical concepts and interpretations can be applied to the measured concentrations of atoms per kilogram for these radionuclides.

Redox potential (Eh) and pH are predicted to strongly affect the solubility of radionuclide-bearing phases and speciation of radionuclides in solution. Studies of the Oklo natural reactor (Curtis and Gancarz 1983) show that sustained radiolysis can lead to localized reduction of multi-valent species (Fe); there is also indirect evidence that radiolysis leads to localized oxidation of complementary multi-valent species (U). A natural analogue study of redox halos surrounding Permian red-bed sediments shows relatively large enrichments in U, Ni, Se, Mo, Pd, and Pb that have remained localized in reducing cores of minerals for millions of years (Hofmann et al. 1987). In a quite different environment, more relevant to low- and intermediate-level waste disposal, the trace element chemistry of hyper-alkaline (pH ~ 12) spring waters located in Oman was studied (Bath et al. 1987). In general, the measured concentrations of Ni, Se, Zr, Sn, Pd, Th, and U were at, or below, the predicted solubilities. One concern in interpreting such data is that the extremely low concentrations observed may reflect trace abundances rather than control by solubility-limiting phases.

4.1.3 Co-precipitation of Trace Radioelements

Essentially all radionuclides are present in trace quantities in nuclear waste forms. Accordingly, it is not expected that each radionuclide (or, more accurately, each radioelement) will form its own, discrete secondary phase; rather, radioelements will be incorporated as trace components in solid solution with alteration phases, such as alumino-silicates, carbonates, sulfates, phosphates, and sulfides. Extending the previous example for cesium, pollucite shows extensive solid-solution behavior with analcite, a sodium alumino-silicate that forms commonly in tests on borosilicate glass. The solubility of a minor component, therefore, cannot be predicted solely on the basis of solubility of individual, end-member phases except for ideal solution behavior. Co-precipitation occurs and must be quantitatively included in assessment of radioelement solubilities.

Co-precipitation, in which trace radionuclides are incorporated into the atomic lattice of a mineral, is a process that could significantly limit release from the near-field (Bruno and Sandino 1987). For example, the precipitation at the leading edge of a moving redox front of reduced uranium (U^{4+}, eight-fold ionic radius of 1.08 Å) in phases such as UO_2 would allow incorporation of other radioelements as a solid solution. Iso-valent species of similar size (e.g., Th^{4+}, 1.12 Å) would show a strong affinity for incorporation into the secondary phase. Non-tetra-valent species (e.g., Am^{3+}, 1.17 Å) and species with greatly different ionic sizes (e.g., Zr^{4+}, 0.92Å) will show a corresponding lower affinity for substitution into the precipitate. This "affinity" corresponds to the Henry's Law partition coefficient (a true K_D) of trace components between the host mineral and the coexisting solution. The theory and systematics for this behavior have been well-substantiated by study of natural minerals co-existing with silicate (Onuma et al. 1968; Philpotts 1978) and aqueous liquids (Volfinger and Robert 1980; Hodder 1983). High affinity leads to K_D values greater than 1, while low affinity relative to coexisting solution leads to K_D values less than 1. Although any incorporation of radioelements into solids will decrease their concentration in solution, K_D values greater than 1 indicate a significant capability for maintaining radioelement concentrations at low levels. Radioelement co-precipitation with potential repository phases, such as iron oxides and calcite, have also been suggested (Bruno and Sandino 1987).

Based on the systematics for trace element substitution, it would be desirable to find a natural analogue in which large, poly-valent elements are rapidly co-precipitated into a mineral structure at low (<100°C) temperature. Interestingly, fish debris composed of biogenic apatite show exactly this behavior (Wright 1990). *In vivo* fish bones show a strongly fractionated pattern for rare earth elements (REE) that are irregularly enriched by 3-4 orders of magnitude compared to sea water (Figure 5). There are two lattice sites in apatite occupied by calcium. Four calcium atoms occupy Ca (I) positions in nine-fold coordination with oxygen from six

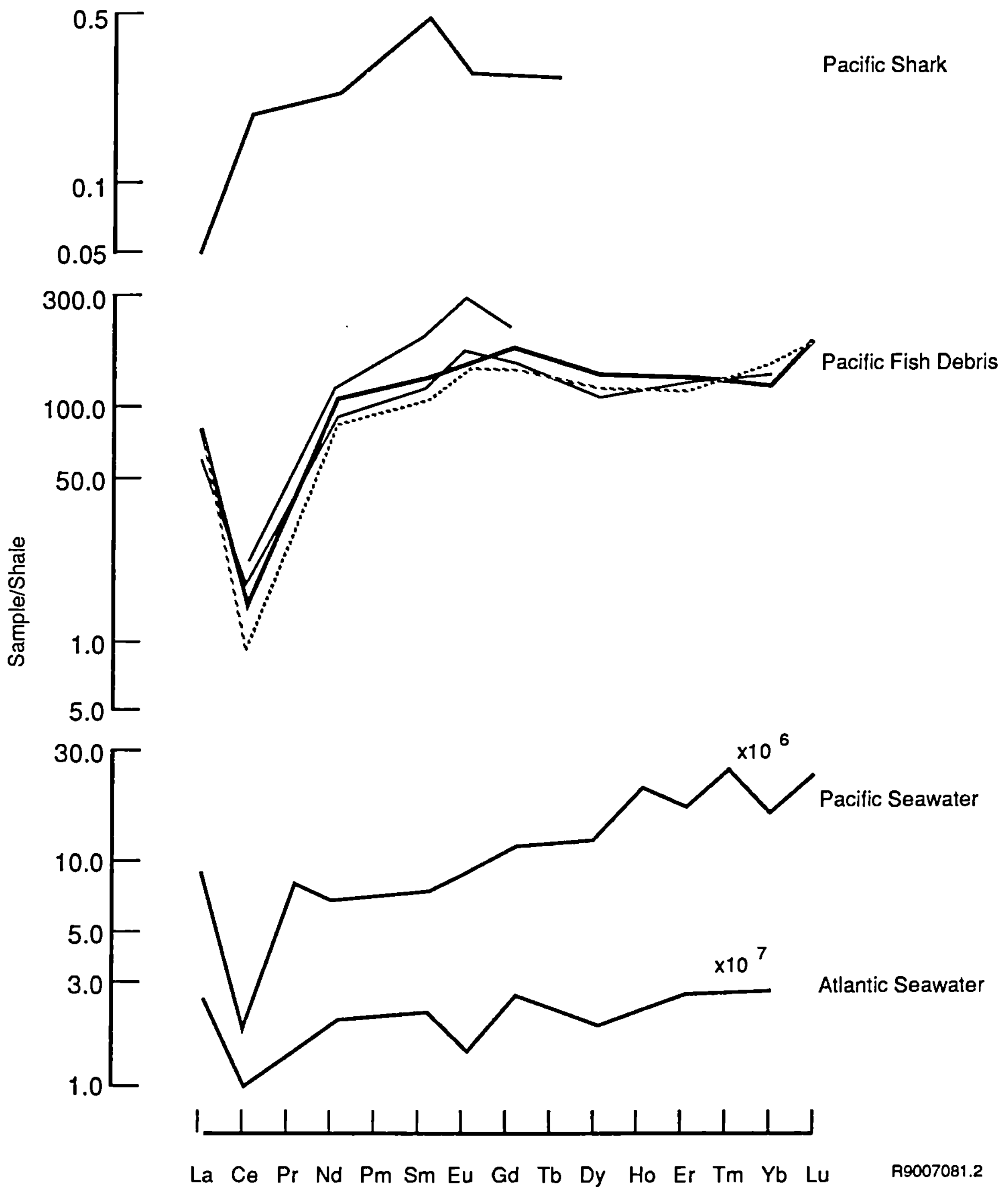


Figure 5. Enrichments of Rare Earth Elements for *In Vivo* and Postmortal Biogenic Apatites Relative to Modern Seawater (Wright 1990).

different phosphate tetrahedra. Six calcium atoms are in Ca (II) positions, an irregular sevenfold coordination with one hydroxyl ion and six oxygens from five different phosphate tetrahedra (Eanes 1973). Substitution of REE, possibly charge-coupled with substitution of mono-valent cations for Ca^{2+} or CO_3^{2-} substitution for PO_4^{3-}, is favorably accommodated at these large lattice sites. Based on Henry's Law and evidence from natural systems, a systematic enrichment of REE in apatite is expected (Irving 1978). The noted fractionated REE pattern of *in vivo* bones is the result of selective biologic mediation during apatite formation.

Postmortal fish bones fall as detritus into the sediment of the sea floor. Examination of modern-day and fossil fish bones indicate that detrital apatite undergoes rapid and irreversible chemical reaction with sea water (Wright 1990). These data further indicate that the apatite becomes strongly and systematically enriched with REE in accordance with crystallographic control predicted on the basis of Henry's Law partitioning. Experiments indicate that postmortal apatites attain partition coefficients with respect to coexisting waters of 10^5 to 10^6 for all REE within a matter of hours (Koeppenkastrop and De Carlo 1990). Furthermore, such enrichments seem to be irreversible, persisting in fossil conodonts found in clay sediments for up to 500 million years (Wright 1990). Other trace elements also show enrichments in detrital apatite consistent with crystallographic control.

The selectivity, magnitude, rapidity, and apparent irreversibility in enrichments of large cations within biogenic apatites have been established from natural analogues. Further laboratory investigation of biogenic apatite as a co-precipitation phase to reduce radionuclides releases from the EBS would seem to be warranted.

4.2 Transport

Diffusion of dissolved radionuclides through compacted bentonite is expected to control release for many EBS designs. Mass-transfer theory for predicting release rates in such systems is exceptionally well-developed and accepted (Pigford and Chambre' 1988). Limited laboratory validation of mass-transfer predictions in simplified EBS geometries have been made (Geldart et al. 1988). In addition, many natural analogues for diffusive migration exist (Chapman et al. 1984). A study of inter-layered marine- and freshwater-sediments in Loch Lomand, Scotland (McKinley et al. 1984) is a noteworthy example in which there is excellent control of the timing and conditions. Results from this study indicate general concordance between predictions of diffusional transport, based on laboratory data and field measurements. This concordance is a necessary, but not sufficient, condition to demonstrate the uniqueness of this interpretation. Interestingly, I and Br appeared to be far less mobile than predicted from a simple model of diffusion. The assumption of colloid filtration by clay material is also qualitatively supported.

The previously mentioned analogue of the bronze cannon embedded in marine clays also presents opportunities for validation of diffusional transport models. In an effort to evaluate the amount of copper released to the sediment surrounding the cannon, the researchers measured the concentration of copper in the sediment as a function of distance. Analyses of copper distribution do show considerable variation with respect to distance from the sediment-ocean interface. Nonetheless, it may be possible to compare these distribution profiles with transport predictions based on the corrosion phases of copper and the known behavior of copper in marine sediments.

5.0 Analogues for Temporal Variation of Parameters

Temporal variation of natural parameters is a central issue in establishing the predictive reliability of the engineered barriers and the near-field. Long-term records of natural phenomena show seemingly erratic behavior on both a short- and long-term time scale. Empirical correlations of many natural phenomena obtained by Hurst using rescale range analysis (Hurst et al. 1965), and later re-interpreted by fractal Brownian motion (Voss 1985), confirm that natural stochastic processes exhibit clear persistent trends. Indeed, a large number of variations in natural phenomena, including thickness of tree rings, river discharges, rainfall, varves, sunspot activity, and temperature, all display the same temporal correlation factor, called the Hurst exponent ($H = 0.72$). An H value of 0.5 represents true Brownian motion (random walk), while H values greater than 0.5 indicate persistent stochastic behavior over time (Feder 1988). Rescale range analysis has been applied to model the initiation of localized failure modes for metals, and to assess expected variation in the composition of repository pore waters and this effect on container failures (Williford 1990).

6.0 Conclusions

High confidence and reliability in isolation of nuclear waste can be achieved by the engineered barriers system (EBS). The long-term, predictive reliability of EBS materials can be tested and validated through studies of natural analogues. Selection of analogues must be predicated on material properties and processes that are relevant to EBS performance.

Excellent natural and archaeological analogues exist to evaluate the stability conditions for metallic copper as a container material. Analogues for corrosion-resistant and corrosion-allowance materials are problematical; they are non-existent for the former and restricted to modes of failure (i.e., uniform corrosion) for the latter that may be overly optimistic compared to failure at weldments for which there are no suitable analogues. Abundant natural analogues exist regarding the smectite-to-illite transition as a function of temperature, starting materials, access of water, and duration. At temperatures below 100°C, a bentonite that is essentially free of initial illite is expected to remain unaltered for more than 10^6 years. Furthermore, if illitization were to occur, the resulting backfill will still be extremely non-conductive and its effectiveness as a diffusion barrier may not be compromised. Natural analogues confirm the expected formation and rate of change for metastable-alteration products (Ostwald step-rule) of engineered barrier materials, notably glass, under repository conditions. Numerous natural analogues are also available to validate the applicability of thermodynamic equilibrium and mass-transfer models in predicting the migration of radionuclides through the EBS.

Extensions of analogue studies for the EBS are needed. The role of natural analogues in guiding experimental work and evaluating the adequacy of experimental apparatuses is often overlooked. In particular, "acceleration" of short-term laboratory tests to collect data under repository-relevant conditions that are representative of much longer durations should be based on these correlations developed from natural systems. Analogues composed of two or more components of the EBS could be used to evaluate the potential for synergistic reactions. The systematic study of trace-element partitioning by co-precipitation under low-temperature conditions is a complex, yet important, issue that could be resolved by natural analogue studies in conjunction with laboratory tests. This is consistent with a necessary emphasis on the "fate-of-radionuclides", rather than merely "fate-of-waste-forms", for near-field performance assessment. Perhaps the best natural analogues would be deeper excavation of potential repository sites. From these, the expected long-term performance of materials under thermally elevated, repository conditions could be determined. Finally, the nuclear catastrophe at Chernobyl and the far less severe event at Three Mile Island might be valuable, albeit tragic, analogues for disruptive scenarios. Certainly these sites contain evidence on the behavior of engineered and nuclear materials under conditions simulating (and exceeding) the effects of a volcanic intrusion through a nuclear waste repository.

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USING HYDROGEOCHEMICAL DATA FROM NATURAL ENVIRONMENTS TO IMPROVE MODELS OF RADIONUCLIDE SPECIATION IN GROUNDWATERS

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ABSTRACT

It is essential that computer-based models used in the safety assessment of radioactive waste repositories accurately represent the processes occurring in real field systems. Confidence in long-term predictions of radionuclide migration will then depend upon the completeness of data available, particularly those obtained from the disposal site, and correct implementation of the model. The study of natural geochemical systems provides information on the adequacy of the underlying "generic" database and enhances our understanding of the transport mechanisms which form the basis of performance assessment. This paper concentrates on speciation-solubility modelling and describes four natural occurrences of uranium, each of which displays a different facet of uranium migration behaviour. The attributes of each site and the means by which uranium is immobilised are described. Retardation is highly species specific and this is illustrated through the use of site data in equilibrium speciation and coupled chemical transport calculations. Oxidation of U(IV) to U(VI) species promotes leaching of uranium ore at all the locations studied, emphasising the need to ensure that reducing conditions persist in a repository dominated by its actinide inventory.

1. INTRODUCTION

Post-closure radiological safety assessments hinge on the ability to predict accurately the likely rate and extent of geochemical transport from a radioactive waste repository to man's immediate environment. Geochemical considerations are not confined to the "far-field" but influence the performance of the backfill, the container and the waste-form, itself. Increasingly, computer-based models have come to occupy an important role in assessment methodology owing to the inherent intractibility of many complex field systems to experimental treatment. Among these, thermodynamic models are used to provide information on radionuclide leaching [1], solubility [2] and the aqueous speciation obtaining for a given set of equilibrium conditions [3]. The latter is crucial as this determines, to a large extent, the tendency of a species to sorb onto mineral surfaces, its bioavailability and, ultimately, its toxicity [4].

Structured procedures for incorporating chemical equilibrium models within a risk assessment framework have been proposed [5] and implemented successfully, at least in trial simulations. In the United Kingdom, for example, they are used both to provide input for probabilistic risk assessment (pra) calculations and to re-examine the cause of high risk pra results (Figure 1). Emphasis now is being focussed towards field studies in an attempt to confirm the accuracy of model predictions.

It is ironic that "Natural Analogues" are being advocated as a means of providing confidence in numerical modelling techniques. Geochemical models were originally developed [6] to aid characterisation of natural systems and to support the results of field observations. Their subsequent use in performance assessment is much more recent and in the case of cement-based repositories, a more tenuous application of the underlying concepts.

The following section summarises briefly the current status of equilibrium modelling and attempts to define the working bounds of extant codes and thermodynamic databases.

2. MODELLING CHEMICAL SPECIATION

Speciation may be defined as the different chemical forms of an element which together comprise its total concentration in a given environment [4]. Each species will vary in its tendency to hydrolyse, sorb or combine with other species depending on size, charge and steric considerations (Figure 2). Thus, a knowledge of speciation is essential to understanding the likely migration behaviour of a contaminant in any disposal situation. The purpose of thermodynamic models is to identify the dominant aqueous species, those solid phases which control solubility and to gauge the sensitivity of the system to perturbations in environmental conditions.

Approaches to modelling chemical speciation have been described comprehensively in a number of excellent articles [7, 8]. All entail minimising the Gibbs Free Energy of a system, either directly or indirectly. The latter is more common, whereby master species are defined for each element in terms of which all complexation and solubility reactions are expressed. Mass action equations of the form;

$$pM + qL + rH = MpLqHr \; ; \; \beta = \frac{(MpLqHr)}{(M)^{p}(L)^{q}\,(H)^{r}}$$

are then substituted into mass balance terms $M_{TOTAL} = \sum_{i}(Mi)$ for each component and the resultant non-linear equations solved numerically. A supporting thermodynamic database comprising formation constants for aqueous species and solubility products for minerals or other solids provides the basis for the equilibrium simulation [8].

Coupled chemical transport programs constitute a special case whereby speciation and solubility are calculated within a mobile aqueous phase. The code may be "directly-coupled" in that it solves compound equations incorporating mass action expressions for each transported species [9]. Alternatively, an indirect approach may be employed with iteration between discrete chemical and transport modules [10]. The two methods are depicted schematically in Figure 3. In the vast majority of cases, local chemical equilibrium is assumed and, thus, the requirement for basic thermodynamic data remains.

The use of chemical speciation models has many advantages. Results may be obtained relatively cheaply, extremely quickly and for systems where, owing to reasons of sensitivity or interference, direct measurement is not feasible [11]. As a result, more than 200 computer codes have now been written for the simulation of aqueous speciation and several have been shown to provide a reasonable approximation of experimental data when used within their frame of reference [12]. Deficiencies are apparent, however, owing to the limited functional scope of current models and the incompleteness of the thermodynamic database [13]. Such shortcomings are most evident when simulating field systems and in the main relate to:-

i) oversimplification of the natural environment through omission of key processes or "homogenisation" of inherent variability.

ii) irreversible or kinetically slow reactions, for example low temperature mineral transformation.

iii) non-attainment of steady-state as a result of mass transfer through supposedly "closed systems".

iv) non-stoichiometry of natural mineral phases and incongruency in precipitation-dissolution reactions.

v) inaccurate or inadequate thermodynamic data

The last point is crucial as many of these data relate to the actinides and other elements of significance in risk assessment.

A number of data compilations have been produced in recent years for the purpose of modelling equilibrium chemistry [e.g. 14, 15]. These databases differ substantially depending on the compiler's requirements and judgement. It is not surprising, therefore, that widely different results have been obtained for common problems [16]. Considerable effort is now being expended to compare the various listings and, where possible, standardise on an agreed set of constants for risk assessment work [14, 17].

Conventionally, these thermodynamic data apply to conditions of 298°K, 1 bar pressure and zero ionic strength (infinite dilution). Methods for correcting the constants to other temperatures, pressures and solution concentrations are described in detail elsewhere [18, 19].

The studies currently underway will undoubtedly increase the level of consistency in database compilation. It is equally important, however, that the databases are enhanced to include all relevant equilibria and to overcome the gaps in data that clearly exist [12]. It is now recognised that while thermodynamic models can aid interpretation of geochemical systems, it is only by studying the natural environment that the applicability of the rapidly improving models and data can be demonstrated.

Come and Chapman [20] identify four areas in which "analogues" can contribute to the modelling process, by:-

- allowing extrapolation of laboratory observations to larger spatial and temporal scales
- placing realistic bounds on parameter values to be used in modelling
- indicating the dominant mechanisms operating in natural systems similar to those envisaged for waste disposal
- representing the net effect of many complex processes operating over protracted timescales.

The use of equilibrium speciation and coupled chemical transport models to study uranium behaviour at four analogue sites is described below. Each study illustrates a different aspect of uranium geochemistry and together the exercises demonstrate the advantage of multidisciplinary research in this area.

3. APPLICATION OF EQUILIBRIUM MODELS TO ANALOGUE SITES

Natural uranium ore deposits are very amenable to analogue studies. They contain high concentrations of actinide and lanthanide elements subject to the effects of changes in the geochemical environment over timescales of up to several million years [21]. Further, not only are U, Th and several rare earth elements (REE) important constituents of radioactive waste, they also serve as chemical analogues for more intractable actinides; for example, Th(IV) for Pu(IV) and U(VI) for Pu(VI).

The geochemistry of U and Th has now been investigated at a number of analogue sites around the world. These studies include; Oman where hyperalkaline springs have been proposed as a cement analogue [22], Oklo, the "fossil reactor" in Gabon where enrichment of pitchblende ore was sufficient to promote fission chain reactions [23] and Cigar Lake, Saskatchewan where, despite the size of the ore body and the conductivity of the host rock, there is no apparent surface expression of the high U levels found at depth [24].

The present paper highlights recent field, laboratory and modelling work at Broubster in Caithness, Scotland; South Terras, Cornwall; Alligator Rivers, Northern Australia and Pocos de Caldas, Brazil. These four examples are described briefly to illuminate important points arising from applications of speciation modelling techniques to diverse geochemical data.

3.1 Broubster

The Broubster site in the far north of Scotland is divided into two geochemically distinct regions by a single-track road running north-south. To the west are sources of uranium; a leached, laminated, partly bituminous limestone of the Caithness Flagstone Group (Middle Old Red Sandstone) which outcrops along the strike of a fault zone conducting U-rich waters to the surface. Drainage occurs downslope from these sources along divergent paths into an area approximately 100m east of the road. Here a post-glacial peat bog forms the sink for transported uranium, accumulating up to 0.1 wt% U. [25] Field work at the site included the collection of groundwaters for chemical analysis, U/Th speciation measurements, and for U/Th decay series determinations. All waters were oxidising (Eh 200 to 420 mV) and slightly acidic (pH 5.3 to 6.7).

Five groundwaters from the peat sink area were passed through a 0.45 micron filter then through a portable chromatographic separation kit [26], before subsequent elution and ICP-MS analysis for U and Th. In all samples the majority (57-99%) of the soluble U was bound to high molecular weight organic acids; only relatively minor amounts were associated with Fe/Mn oxyhydroxides or in the cationic uranyl form [3]. The analytical recovery for Th was poor, indicating the presence of colloids but the results did suggest that the bulk of the Th present was associated with Fe/Mn oxyhydroxides.

Uranium speciation was modelled with PHREEQE [27] and two sets of thermodynamic data, the preliminary database from CHEMVAL [12] and a NEA compilation based largely on the work of Schweingruber [15]. In the absence of organic matter, the results obtained with the two sets were similar [3]. No U(IV) species were predicted and the uranium concentrations were not solubility controlled, the waters showing clear undersaturation with respect to the common secondary U minerals. U(VI) carbonates were the most abundant species, hydroxyl and sulphate complexes never exceeding 10% of the total concentration. Scoping studies indicated that HPO_4^{2-} levels of 100 ppb would be sufficient for $UO_2(HPO_4)_2^{2-}$ to displace $UO_2CO_3^0$ as the dominant complex [3].

Uranium-humate speciation was modelled initially [3] assuming that all organic carbon is present as humic acid, that aqueous complexation takes place via a straightforward metal-ligand ion-association reaction and that humic acid is completely dissociated ($\alpha = 1$) with a unit negative charge at the soil water pH of 5 to 7. Using the CHEMVAL database and U-humic acid formation constants from Shanbhag & Choppin [28] ($\log\beta_1 = 7.67$ and $\log\beta_2 = 11.57$) there was a pH 'edge' between 5.3 and 6.3 (Figure 4) over which uranium-humate complexation decreased from around 100% to zero as the carbonate ligands competed more successfully for U(VI). Using the NEA-derived database [15] and humic acid formation constants from Kim [29] ($\log\beta_1 = 6.3$ and $\log\beta_2 = 10.2$) a parallel curve was obtained but the pH edge shifted upwards by two pH units (Fig. 4). It was concluded that in acid waters 'humic acids' can compete successfully with carbonate ligands, but that uranium-humate complexation is strongly pH dependent over the range pH 5.5 to 7.5.

In contrast to the above, thorium was predicted to be slightly supersaturated in all samples, along with amorphous iron hydroxides lending support to the premise that co-precipitation on such phases is the most likely means of thorium abstraction from solution [3]. Laboratory studies are now underway to confirm these predictions [30].

Without doubt, equilibrium speciation modelling at Broubster has proved successful in elucidating the dominant processes controlling actinide mobilisation and fixation. A conceptual model was formulated involving the oxidation and release of U from the source horizons, advection downslope and fixation in peat organics. Preliminary modelling efforts also served to focus the requirements of the site investigation programme.

Nevertheless, a number of concerns were raised by this uranium study. The inadequacy of modelling organic-uranium interactions as simple ion-association reactions have been highlighted, with speciation results varying significantly according to the uncertainty in formation constants used. Subsequent work on the portable sequential chromatographic method [26] showed an incomplete understanding of the performance of the DEAE and ion exchange resins when employed in series; current studies are relying on single-step resin separations for more accurate data. The detection limits for dissolved phosphate anions also need to be improved. The findings for thorium raise the related problems of colloid transport and co-precipitation, two processes that are not directly handled by current speciation codes, and for which a sound theoretical basis has yet to be established.

3.2 South Terras

Active migration of uranium is also occurring in the vicinity of the South Terras mine in Cornwall, SW England [31]. Pitchblende ore in spoil heaps abandoned over 60 years ago provide a source of leached U in the groundwaters flowing towards a small stream draining into the R. Fal close by. Recent interest in the site has focussed on the collection and analysis of groundwaters and sediments between the heaps and the stream in order to measure the U plume as a function of depth and distance from the heaps [32]. The alluvial deposits have been found to act as an efficient sink or retardation barrier for U migration.

Thermodynamic equilibrium modelling was used to describe solubility and speciation trends for U and Th as a function of pH, Eh, phosphate, carbonate and organic concentrations [31]. The groundwaters had roughly constant major ion concentrations over the sediment volume sampled precluding substantial variation in U and Th speciation. All the PHREEQE simulations were performed with the CHEMVAL Stage 2 database [12]. The main aqueous U complex in each soil water was predicted to be the U(VI) phosphate, $UO_2(HPO_4)_2^{2-}$, with subordinate uranyl carbonates. To take account of current uncertainty in the phosphate analyses, a parallel series of simulations were carried out in which levels of this key ligand were constrained. In this case, $UO_2(CO_3)_3^{4-}$, $UO_2CO_3^0$ and $(UO_2)_2(OH)_3CO_3^-$ became the dominant species [31]. As expected, thorium was much less sensitive to variations in environmental parameters than uranium, with the $Th(OH)_4^0$ species predominant in all samples.

The soil waters were predicted to be strongly undersaturated with respect to both the primary ore, (uraninite/pitchblende) and secondary alteration U minerals, such as autunite ($Ca(UO_2)_2(PO_4)_2.12H_2O$), saleeite ($Mg(UO_2)_2(PO_4)_2.12H_2O$) and zippeite ($(UO_2)_3(SO_4)_2(OH)_2.8H_2O$). The findings suggest that uranium is being actively leached under present day conditions and imply that direct precipitation of uranium phases along the flow path is unlikely. Some form of sorption, therefore, must be responsible for U retardation.

These speciation calculations have defined the likely mobile U-species and confirmed the mechanism of sorption. The availability of quantitative hydrologic data [31] allowed coupled chemical transport of U migration between the spoil and the stream. CHEMTARD [33] was used to describe the migration of U through the sediments with uptake based on a surface complexation approach [34]. These thermodynamic *a priori* calculations simulated the observed results well without recourse to the simplistic reversible K_d concept [32].

3.3 Alligator Rivers

The Alligator Rivers Analogue Project (ARAP) was established in order to investigate the processes responsible for the long-term geochemical evolution of the Koongarra uranium deposit in Northern Australia [35]. Of particular interest is the widespread occurrence of secondary uranium minerals in weathered rock and the presence of a dispersion fan extending some 80 metres "downstream" of the primary ore (Figure 5).

The mineralised area may be subdivided into four zones:-

- the primary ore body (pitchblende/uraninite)
- a U-silicate zone formed by *in situ* alteration of uraninite
- a secondary uranyl phosphate zone above and downstream of the primary ore
- a region in which lower concentrations of uranium are dispersed within weathered rock and occur in association with clays and iron oxyhydroxides.

Emphasis in geochemical modelling studies to date has focussed on processes leading to formation of the uranyl phosphate zone. Under present day conditions, all secondary ore minerals appear to be actively leaching, given the degree of undersaturation observed with respect to saleeite ($Mg(UO_2)_2(PO_4)_2.12H_2O$ and the other autunite group minerals [36]. This is consistent with a spreading of the dispersion fan, the leading edge of which has an estimated age of 350,000 years [35]. Attempts are now being made to constrain the range of conditions necessary for formation of the uranyl phosphates in the past.

The reaction path tracking capabilities of the EQ3/6 code [37] have shown that rapid release of magnesium and phosphorus relative to leaching of primary ore is necessary to induce saleeite precipitation prior to formation of apatite or non-phosphate bearing minerals, such as uraninite (UO_2) or uranophane ($Ca(UO_2)_2Si_2O_7.6H_2O$). However, the results of such calculations are necessarily dependent on the accuracy of available thermodynamic data. A review of recent thermodynamic compilations intended for risk assessment purposes has shown that the CHEMVAL Database [12] contains values for only two of the secondary uranium places present at Koongarra (saleeite and torbernite) whereas several alternative listings [e.g.17, 38] contain no relevant solubility data, whatsoever. Given that all of the secondary uranium minerals observed were formed by alteration of UO_2, an important component of intermediate level waste, this represents a serious omission. Thus, although much remains to be done at ARAP with respect to quantifying the transport processes operating, the study has already served a useful purpose in highlighting inadequacies in extant thermodynamic compilations.

In the event, many of the lacunae in the CHEMVAL Database and other compilations could be remedied by comprehensive review of the available literature [36]. Nevertheless, several uranium - bearing solids have been identified at the site for which no reliable data exist. The use of extrapolation techniques in such cases is unavoidable and has been shown to be a pragmatic solution in the absence of direct measurement [13, 18].

Finally, the abundance of U(VI) phosphates at Koongarra has again focussed attention on a key issue in uranium groundwater speciation; the relative stability of U(VI) carbonates and phosphates [39, 40].

3.4 Pocos de Caldas

Modelling studies based around the Pocos de Caldas analogue are reported elsewhere at this workshop. The following serves only to place this site in context with respect to speciation work at the locations discussed previously. Pocos de Caldas differs from the three other examples considered in that U(VI)/U(IV) redox precipitation has been shown to play a significant role in uranium immobilisation within the groundwater system [41]. This contrasts with fixation by organics (Broubster), iron oxyhydroxides (South Terras) and precipitation of secondary uranyl phosphates and silicates (Alligator Rivers). Even at Pocos, however, sorption of cationic U(VI) hydroxy species is perceived to be important in oxidised rock [42].

A substantial amount of geochemical and hydrologic data has now been gathered at Pocos de Caldas. In the region of a redox 'front', localised remobilisation of uranium is occurring where oxidising waters are brought into contact with strongly reducing bedrock. This has resulted in dissolution and re-precipitation of pitchblende nodules in narrow mineralised zones and uranium concentrations of up to 3% have been measured in whole rock analyses as a result of concretionary nodule formation [41].

Several attempts have been made to represent the movement uranium across such a redox front. These studies vary considerably in approach and include both pseudo-kinetic [43] and local equilibrium [44] methods, as described in an accompanying paper [45]. However, the models agree in important respects and have elucidated the dominant mechanisms operating. For example:

- uranium speciation is dominated by hydroxy complexes owing to the extremely low concentrations of competing ligands.

- coupled calculations predict uraninite accumulation in a narrow zone in reduced rock, a few centimetres "behind" the front.

- in the absence of net advective flow, the redox front itself is stationary.

The above findings are consistent with the known occurrence of uranium in the Osamu Utsumi mine [41] and provide a clear demonstration of the usefulness of speciation modelling techniques in unravelling the geochemistry of complex natural systems.

4. IMPLICATIONS FOR RISK ASSESSMENT

Quantitative validation of long-term predictive models by recourse to natural systems is not a realistic aim owing to the complex interaction of the processes operating and the difficulty in constraining boundary conditions [46]. Further, no single site can reasonably be expected to display the manifold features of an engineered radioactive waste repository. The usefulness of analogues stems from the fact that they remain the only means of observing the net effect of geochemical *processes* acting over timescales appropriate to a safety assessment.

Although estimates of elemental solubility can be obtained and compared directly with model predictions, evidence of chemical speciation in the natural environment is largely circumstantial. In actuality, the modelling process is iterative with early analyses used to construct preliminary conceptual models which, in turn, prioritise data requirements needed to refine the model [3, 30]. The examples described in this paper illustrate the application of such modelling techniques to interpreting natural occurrences of uranium.

Collaborative field, laboratory and modelling studies within the Natural Analogue programme are helping to formulate a coherent picture of uranium behaviour in the terrestrial weathering environment. Oxidation of U(IV) to U(VI) species is responsible for mobilisation at each of the four sites discussed; acting as a "trigger" for release mediated by complexation with carbonate or other anions. The mechanisms of immobilisation differ, however, and several may operate in concert at any given site, depending on ambient conditions. For example, at Pocos de Caldas, reduction of U(VI) promotes uranium fixation but only in the region of the redox front [41]. Sorption of uranyl species onto iron oxyhydroxides is the dominant mechanism in oxidised rock and volumetrically such oxides may represent the major sink for uranium in the shallow weathered zone [44]. Similarly, at Koongarra, precipitation of secondary uranyl phosphates is important in the immediate vicinity of the main ore body but fixation on oxides impedes further progress of the uranium plume "downstream" along the dispersion fan [35]. In both cases, the bulk of U transported is in true solution and amenable to conventional thermodynamic treatment, provided, of course, transport is slow relative to reaction rates.

In addition to generating a better qualitative understanding of geochemical processes, the areas where analogue data have contributed substantially to current risk assessment capabilities include:-

i) *Thermodynamic Database.* The Alligator Rivers and South Terras exercises, in particular, have identified shortcomings in thermodynamic listings compiled for risk assessment purposes. Together with knowledge of the inventory and known radiochemistry natural system studies provide a means of prioritising future data requirements.

ii) *Functional Scope of Models.* The Broubster study highlighted the requirement for a more comprehensive model of actinide-humate binding [3]. Further work is needed to better quantify such processes and to address a number of geochemical mechanisms for which the theoretical basis has yet to be established. Examples include groundwater colloid formation and transport, incongruent leaching of metamict phases and the various processes commonly grouped under the general heading "sorption".

iii) *Improved Site Investigation Techniques.* The use of analogue data for testing quantitative thermodynamic models has pinpointed deficiencies in current analytical methods. Areas of concern include the sensitivity of groundwater phosphate assays [35], the selectivity of chromatographic techniques [26] and, not surprisingly the establishment of oxidation-reduction conditions [41].

Without doubt, the widespread proliferation of advanced numerical models in recent years has far outstripped development of the underlying thermodynamic database and, in some cases, current understanding of natural processes.

It is essential, therefore, that assessment modelling draws on relevant geochemical experience and that sight is not lost of where disposal will actually take place. Modelling can provide a focus for field-based studies and should be carried out in conjunction with site investigation wherever the opportunity exists.

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Figure 1

Chemical Models in radiological risk assessment methodology

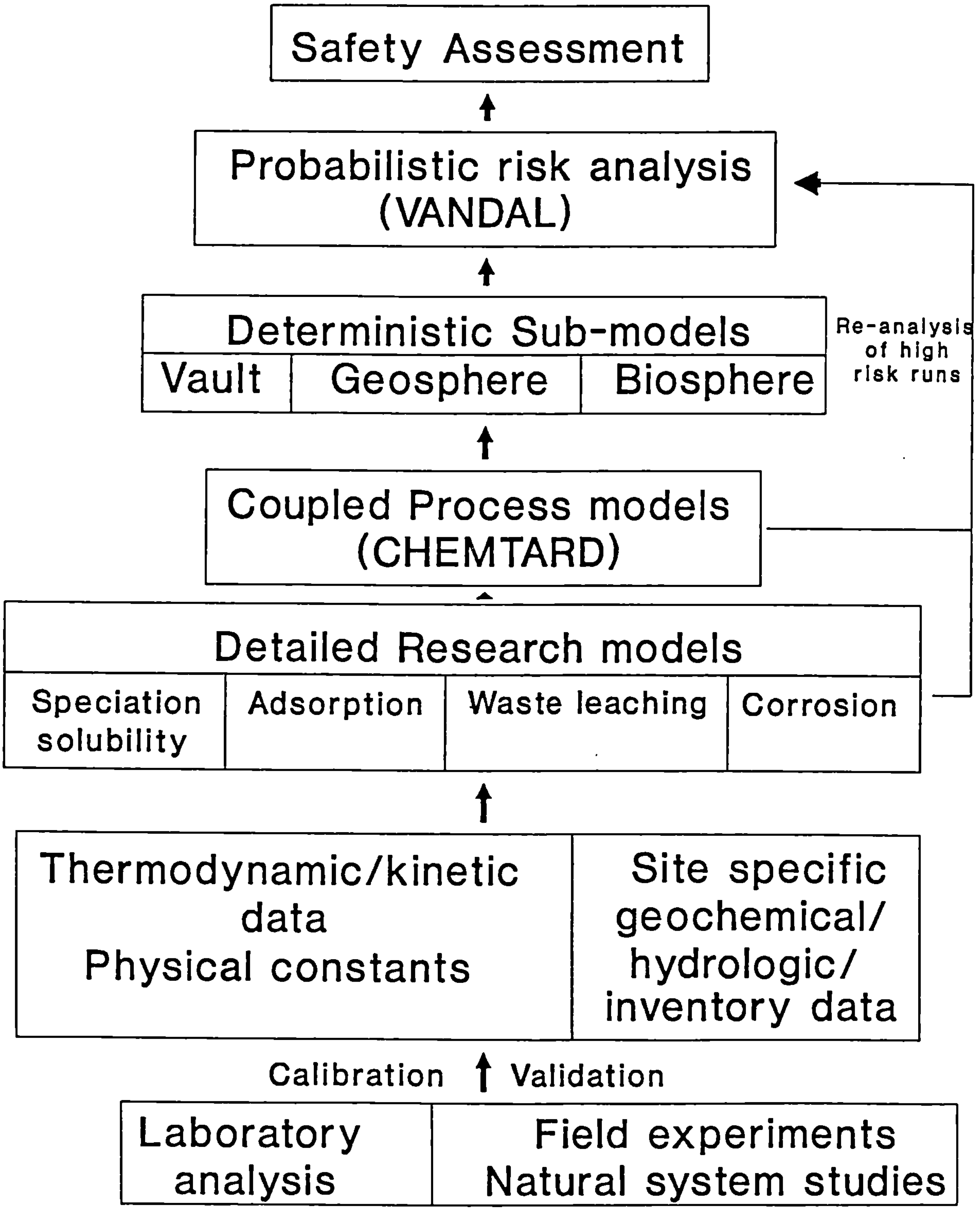


Figure 2

Speciation of metal ions in Natural Waters

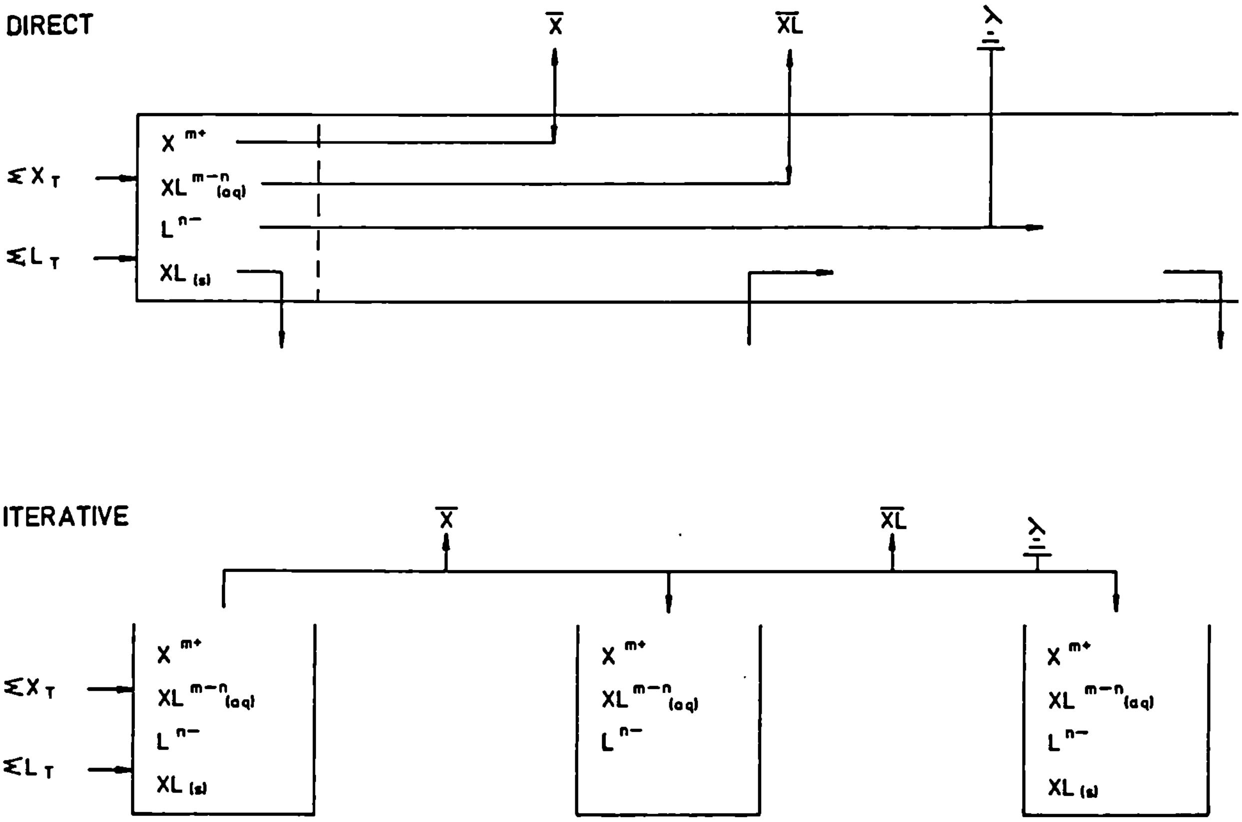
1 nm 10 nm 1000 nm

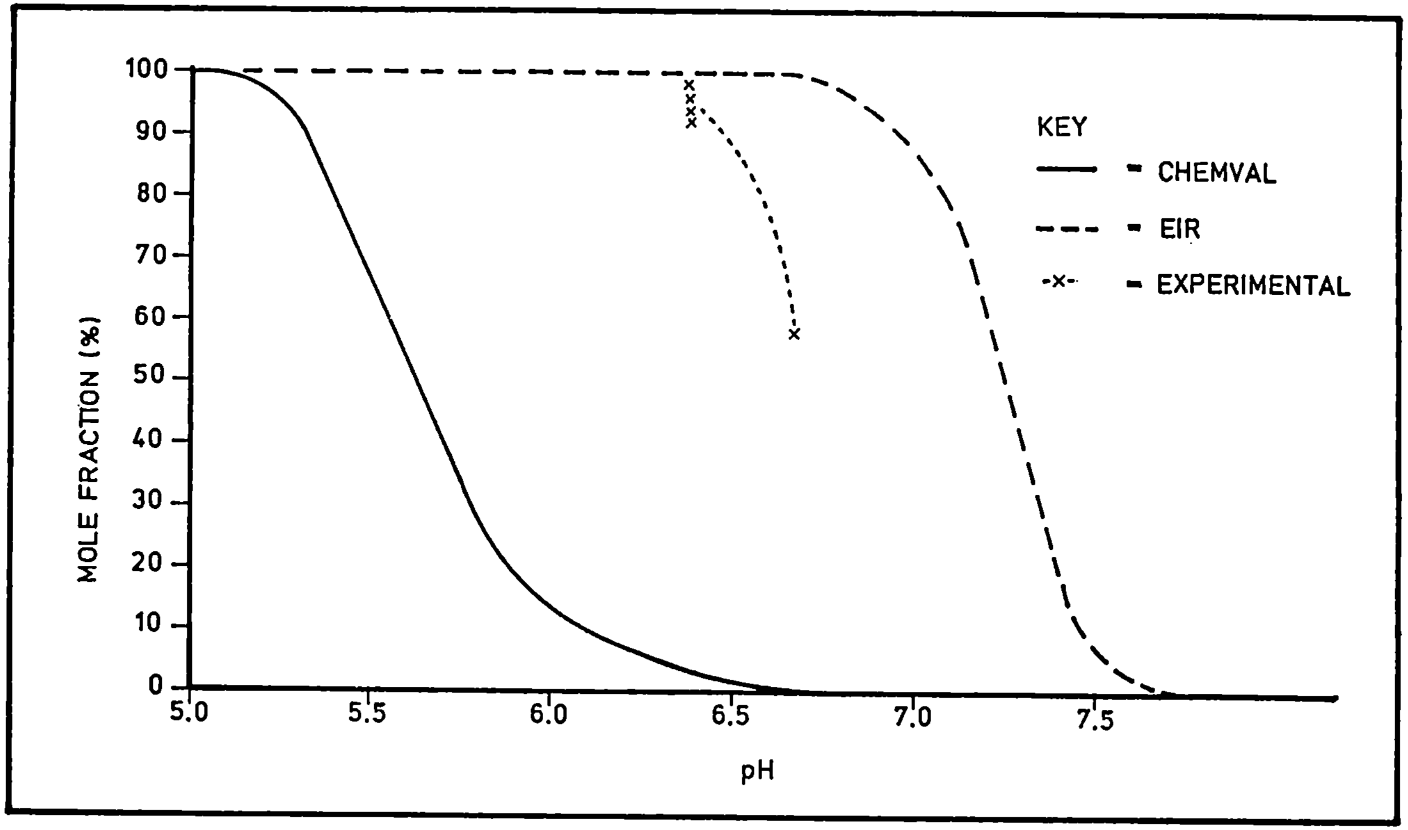
Soluble Colloidal Particulate

Metal Species	Free Metal Ions (aq)	Inorganic Ion pair Organic Chelates	Organic Complexes	Metal Species bound to High Molecular Weight Organic Material	Metal Species Adsorbed on Colloids	Metals Incorporated into Organic Particles and Remains of Living Organisms	Mineral Solids Metals Adsorbed on Solids; Precipitates, Co-Precipitates
Example	$(X^{n+})_{aq}$	XSO_4^{n-2}	X-fulvic $XEDTA^{n-4}$	X-humic acid	$X\text{-}Fe(OH)_3$ $X\text{-}MnO_2$	X-organic solids	X-clay

Figure 3

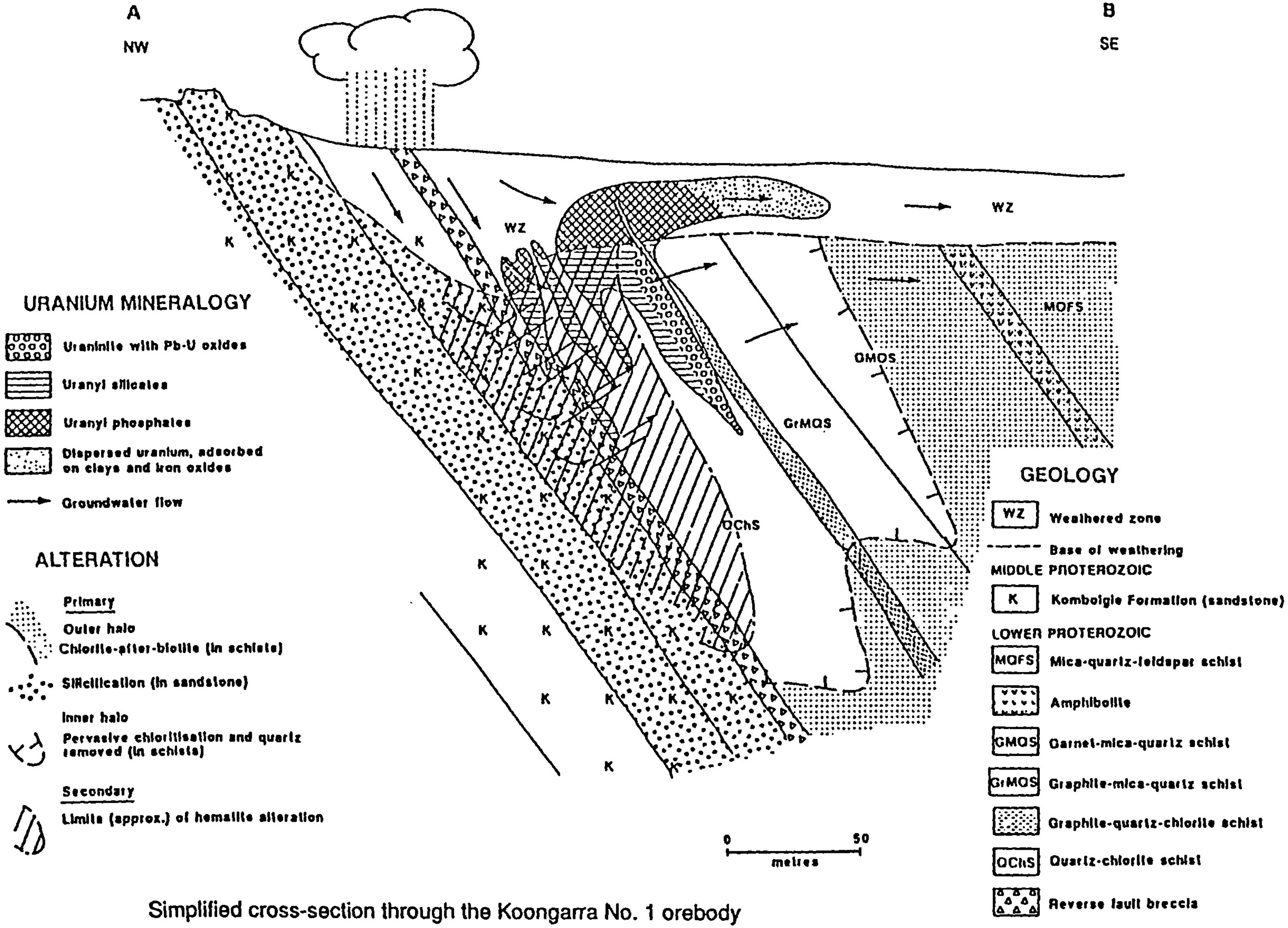
SCHEMATIC DESCRIPTION OF DIRECT AND ITERATIVELY COUPLED MODELS





U-HUMATES IN BROUBSTER SOIL WATERS

Figure 4



Simplified cross-section through the Koongarra No. 1 orebody

Figure 5

NATURAL ANALOGUES IN PERFORMANCE ASSESSMENT: IMPROVING MODELS OF RADIONUCLIDE TRANSPORT IN GROUNDWATERS BY STUDYING THE NATURAL ENVIRONMENT

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ABSTRACT

This paper reviews studies of solute transport in groundwaters which have attempted to derive information relevant to modelling the performance of nuclear waste repositories. The literature of such natural analogue studies is quite extensive but, on close inspection, it can be seen that much represents fairly academic geochemical work in which the link to nuclide transport models is tenuous or, indeed, incorrect. However, when careful attempts have been made specifically to test such models, there is little indication that the performance assessment fraternity have taken any account of the conclusions drawn therein. Several examples are provided to support this thesis although it should be noted that it is impossible to cover all fields of interest in a review of this nature.

INTRODUCTION

One of the most difficult aspects of the safety analysis of a radioactive waste repository is the description of the migration behaviour of any radionuclides released from the encapsulated waste. Such studies are generally based on the extrapolation of data from short term laboratory (and, occasionally, field) experiments to the much longer time scales of interest to performance assessment modellers. It is additionally extremely difficult, if not impossible, to recreate (in anything approaching a realistic manner) the highly complex system which constitutes a repository and its environs. Nevertheless, safety assessment requirements are clear and such predictions must be made.

The usual way to carry out this task is to employ a transport model which describes, mathematically, groundwater transport along with those processes which retard any given dissolved species (with respect to an ideal, non-reacting solute). Such models attempt to define boundary conditions and use input functions which are constrained by the environment under examination. Most rock-water systems are extremely complicated, however, and so defy rigorous definition by a model. Simplifying assumptions are then necessary, (many of which are never clearly stated) and the great danger is that the model description becomes too simplistic and fails utterly to address the problem areas of greatest interest (many of which are of concern mainly because of their very complexity). Natural analogues (any process occurring in the natural environment which is seen to be analogous to mechanisms considered important in the long term containment of radioactive waste; referred to simply as "analogues" for the remainder of this discussion) can be of great use in this context.

Analogues may be the only way of obtaining relevant data on the cumulative effects of radionuclide migration in groundwaters over the time scales of interest to repository performance assessors (≈10^3-10^6y). The use of analogues to provide assurance that radionuclides (released from a radioactive waste repository to groundwaters) will actually behave as stated in predictive assessment codes has wakened the interest of modellers who deal with the dispersal of radionuclides throughout the environment. In their most basic form, analogues are of use in constructing performance assessment models by indicating which of the naturally occurring processes impact on repository design and function (Chapman et al., 1984). Analogues can, therefore, assist in developing the conceptual models by specifying the boundary conditions and providing data. In the course of developing models, analogues are of particular use, especially in the case of coupled processes because the natural environment is inherently interactive and so provides a self consistent database (IAEA, 1989). Such uses of analogues are well documented (e.g. Nagra, 1985; Côme and Chapman, 1987; McKinley, 1989) and of proven use.

A more contentious, but nevertheless crucially important, use of analogues is in the validation of performance assessment models. It has been argued (especially by modellers) that analogues cannot possibly be of use in model validation because the data produced is inherently complex and often vague. It is further stated that data produced in laboratory experiments is inherently better because the parameters are precisely stated and results are produced with good, quotable errors. Such beliefs are partly a matter of attitude: surely a nice, clean laboratory must produce "harder", more accurate data than, for example, the examination of U migration in a wind-swept smelly peat bog? This conveniently ignores the fact that, to date, many laboratory (and field) experiments have been carried out under totally unrealistic conditions which in no way whatsoever can be related to the conditions of, and processes in, a repository sited deep underground. What can be the possible justification of, for example, an experiment which purports to examine U sorption deep in a fractured anoxic rock formation which is carried out on a laboratory bench with finely crushed rock and synthetic (possibly oxidising) groundwater?

The purpose of the discussion presented here is not, however, to criticise laboratory experiments (adequately covered elsewhere; e.g. Bradbury and Jefferies, 1985) but rather to examine the rôle of analogues in improving performance assessment models of radionuclide transport in groundwaters, especially in the potential validation of those models. In the case of chemical solubility and speciation data, there are numerous examples of the use of analogues to validate thermodynamic databases (see the review of Read and Hooker, 1990) and, although such (positive) examples may not be so readily available in the field of radionuclide migration, at least validation of the model assumptions is equally important (Chapman, 1988).

THE TREATMENT OF RADIONUCLIDE MIGRATION IN GROUNDWATERS IN PERFORMANCE ASSESSMENT CODES

Before entering into the description of the uses of analogues in the study of radionuclide migration in groundwaters it is, perhaps, apt to briefly outline the structure of the models used in performance assessment codes with comments on the inherent assumptions and problem areas. Much of this description summarises McKinley and Hadermann (1984) and a wider ranging discussion is contained therein.

Solute transport

In most cases, radionuclide migration is assessed by means of a (geosphere) transport model which attempts to describe groundwater transport mathematically. Both advection and hydrodynamic dispersion are considered along with those processes which produce retardation of given dissolved species with respect to an ideal, non-reacting solute. The first step, then, is a description of groundwater flow on a regional scale, based on hydrogeological information on infiltration rates, permeabilities, hydraulic heads and such like. It is important to realize, however, that while these parameters are useful, they do not describe the groundwater system in enough detail for a transport model to be defined. Additional information such as the physical nature of the flow zones (fracture connectivity, extent of non-flowing porosity etc.) is required because solute transport is affected by diffusive and dipersive processes as well as advection and also by interaction with available surfaces.

In order to then produce a quantitative mathematical model of solute transport, all of the above data must be reduced to manageable proportions, generally by means of the REV (representative elementary volume) concept (e.g. Bear, 1979). This corresponds to a macroscopic "unit cell" which contains, in the smallest possible volume, all processes occurring in a given section of flow path and involves the assumption that average flow properties are reasonably constant when varying the REV size. A mass balance equation can then be written when a REV has been geometrically defined. In an ideal homogenous, anisotropic saturated porous medium, the transport of a solute which does not interact with the solid phase (and where diffusion into dead-end pore spaces is not considered) may be described by:

$$\delta/\delta t\ (\epsilon C_w) = -\ \vec{\nabla}\epsilon\ (C_w\vec{V} - \underline{D}\ \vec{\nabla} C_w) \qquad (1)$$

where
C_w = the solute concentration in the aqueous phase (mol m^{-3})
$\underline{\epsilon}$ = the effective (or available) porosity
$\vec{V}$ = the water velocity field (m s^{-1})
$\underline{D}$ = the hydrodynamic dispersion tensor field ($m^2 s^{-1}$)
$\vec{\nabla}$ = the vector differential operator (m^{-1}).

Additional terms can be included to take into account radioactive decay or ingrowth and, after defining initial and boundary conditions for Cw, the above equation can be solved for any ϵ, V and D. Further simplifications are often made, such as considering flow in only one or two dimensions or assuming idealised geometry for the flow systems.

Sorption processes

Of course, potential repository host rock formations do not consist of inert, porous media and most solutes react with the solid phase in some form to decrease the rate of solute transport relative to the aqueous medium, giving rise to an observed retardation. The actual processes involved in the retardation are complex and include the chemistry of the rock-groundwater system as well as the structure (both on a micro and macro scale) of the flow path.

The more important retardation mechanisms are illustrated in Figure 1. Physical processes are shown in Figures 1a and 1b where diffusion into dead-end porosity and filtration and ion exclusion are detailed respectively. The former process can be extremely important in the case of advective transport in fissured rock and is dependent to some extent on the solution chemistry (i.e. solute size and charge). Other important processes, which involve direct binding of the solute to the rock surface, are illustrated in Figure 1c. Generally considered together as sorption, the examples presented include physical sorption, ion exchange and mineralisation. Precipitation of new phases (Figure 1d) could be considered, along with coprecipitation, as the end-member of the sorption sequence shown in Figure 1c.

All of the above mentioned retardation mechanisms occur to some extent although it is often difficult to estimate their relative importance for any particular reacting solute. Large simplifications are thus introduced to derive REV's and subsequent mass balance equations. This could be achieved by including kinetic terms for sorption and desorption into the general transport equation (1), e.g.

$$\delta/\delta t\ (\epsilon\ C_w) = -\ \vec{\nabla}\ \epsilon\ (C_w\vec{V} - D\ \vec{\nabla}\ C_w) - K_1\epsilon\ C_w + K_2\ \rho\ C_R \qquad (2)$$

where

C_R = the concentration sorbed on the rock phase (mol kg^{-1})

K_1 = the sorption rate constant (s^{-1})

K_2 = the desorption rate constant (s^{-1})

ρ = the bulk rock density (kg m^{-3})

and with the assumption of first order kinetics and ignoring decay/ingrowth.

The rate of change of the rock phase radionuclide concentration can be incorporated so:

$$\delta/\delta t\ (\epsilon\ C_w + \rho\ C_R) = -\ \vec{\nabla}\epsilon\ (C_w\vec{V} - D\ \vec{\nabla}\ C_w) \qquad (3)$$

assuming that any transport in the solid phase can be neglected (c.f. Rasmuson and Neretnieks, 1983).

In order to solve the above equations a (further) simplification is often made with C_R taken to be a simple function of Cw viz

$$C_R = Kd \cdot C_w \qquad (4)$$

where Kd is the distribution coefficient (m^3 kg^{-1}) and assuming the reactions involved are very fast.

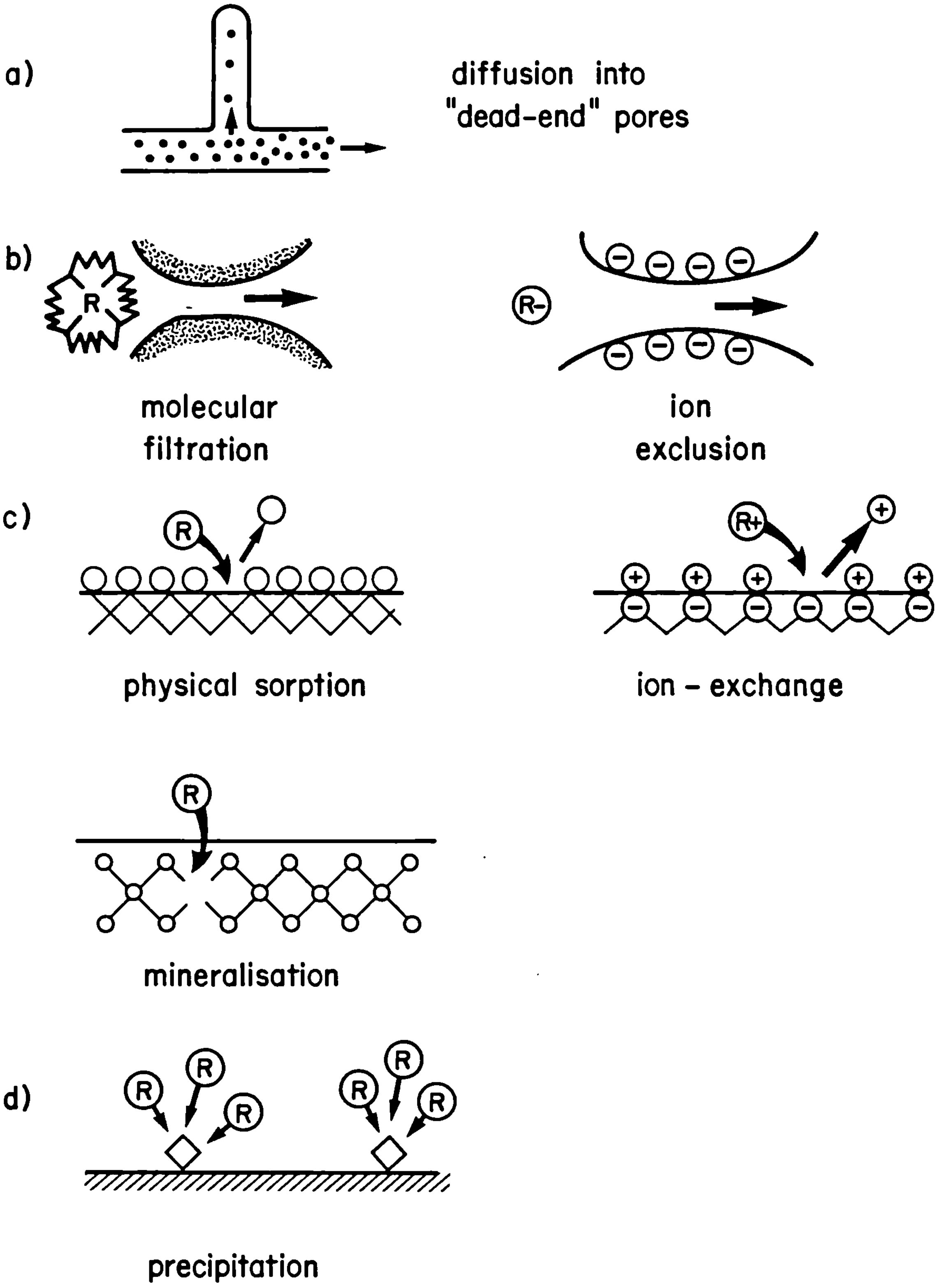

Figure 1: Some of the more important retardation mechanisms for radionuclide migration in groundwater: a) and b) detail solute transport processes while c) and d) represent sorption processes (after McKinley and Hadermann, 1984)

Unfortunately, the Kd nomenclature in the area of pollutant transport studies is "horrendously confused" (McKinley and Hadermann, 1984) but, in the case of the transport models under consideration here, is usually taken as an empirical representation of kinetically fast, concentration independent, reversible sorption. Sorption is, in fact, often found to be a function of concentration and so is better defined by an isotherm such as that of Freundlich (1926) where

$$C_R = \alpha \, C_w^{\beta} \qquad (5)$$

where α and β are empirical constants.

Such an isotherm can, in principle, be included in the transport equation and an example of such a model has been published recently (Jakob et al., 1990). This does, however, make solution of the, now non-linear, equation much more difficult and, in practice, the much simpler Kd approach of equation (4) is currently utilised in repository performance assessment. For this application, Kd values can be derived which take concentration dependance into account in a conservative manner (McKinley and Hadermann, 1984).

It can, therefore, be seen from the above discussion that most transport models presently utilised in predictive performance assessment codes employ extremely basic representations of the process in the natural environment which they attempt to define mathematically. How, then, can analogues, which are usually studies of highly complex, multi-process features be of use in improving the representation of radionuclide migration in groundwaters in present geosphere transport models?

ANALOGUES: THEIR USE TO IMPROVE THE DESCRIPTION OF RADIONUCLIDE MIGRATION IN GROUNDWATERS IN GEOSPHERE TRANSPORT CODES

In their most immediate forms, analogues are intrinsically useful to geosphere transport modellers by simply illustrating many of the processes which will be of significance in radionuclide migration in groundwaters. Analogues can also be used to define the conceptual models which constitute the transport codes and, most importantly, to validate those codes. It has been argued that, due to their intrinsic complexity, analogues can never truly quantitatively validate transport models (IAEA, 1989). This may well be an irrelevant point as, in many instances, analogues will be the only possible approach to validate models; laboratory experiments simply cannot simulate the complexity required to even realistically investigate many of the processes involved, never mind attempt to validate them.

Certainly, many analogue studies carried out to date are of little or no use for model validation as they are either too superficial in their approach or do not address the questions of importance (too many are merely interesting geochemical studies tacked on to a radwaste programme as an afterthought). Equally, many other studies can offer no more than semi-quantitative validation, again for the reasons given above and/or the process studied was simply too complex for easy quantification (e.g. colloid transport). Nevertheless, such studies may produce information leading to modification of the mathematical description of radionuclide migration as encoded in the geosphere transport models. Other studies have led to validation of certain models or, more often, certain specific aspects of given models. In the following discussion, several examples from an extensive body of literature will be examined in an attempt to indicate the use of analogues to improve the modelling of radionuclide migration in groundwaters.

Macroscopic description of groundwater transport

Regional groundwater studies and models specify the large-scale groundwater fluxes which provide the boundary conditions for the microscopic (local) models but also may be used directly to determine radionuclide transport through porous aquifers (after release from a low permeability host rock) or the extent of dilution in such aquifers. Although the approaches used in such work are part of classical hydrogeology, the extrapolations in space and time required for repository performance assessment are quite unusual.

One of the few studies to have tested the applicability and validity of transport models on a regional scale is that reported by Pearson et al. (1983) and Andrews and Pearson (1984). Here, in the well characterised Carrizo aquifer of Texas, in which flow occurs in a porous sandstone bounded by well defined aquitards, an attempt was made to validate the relatively simple transport model SWENT (Intera, 1983). The model is basically the same as the simplified transport model discussed above but, rather than using the Kd terminology applied here, a retardation coeffecient (R) is employed where, in the case of one dimensional advection,

$$R = 1 + (\rho\ Kd/\in) = V_w/V_n \qquad (6)$$

where:

V_w = mean velocity of the water (m s^{-1})

V_n = mean velocity of the solute (m s^{-1})

In this example the measured distribution of the "non-retarded" (by definition in the treatment) C-14 along a 100 km section of the aquifer was compared with that predicted by SWENT. Other data required by the model were input directly from parameters measured in the aquifer (e.g. density, porosity, etc.) and the excellent fit between the measured and predicted C-14 (Figure 2) was accepted by the authors as providing validation of the model. To further test the model, measured U-234/U-238 activity ratios (representing retarded U) in the aquifer were compared with those predicted by SWENT. Here the decrease in the activity ratios with distance in the aquifer were taken as a measure of the rate of U movement in the aquifer, which is related to the rate of groundwater movement via the R (or Kd) factors of equation 6.

The model results were compared with the observed data for those points below 33 km in the 100 km section (Figure 3) and an in-situ Kd obtained for U (best fit ≈6 ml g^{-1}). It is difficult to find directly comparable laboratory data, but a conservative Kd for U of about 10 ml g^{-1} seems reasonable for a reducing, quartz-rich sandstone such as the modelled section of this aquifer (c.f. Wittwer and McKinley, 1990). This indicates that the retardation of U is reasonably well represented by the SWENT model in this instance. The Carrizo aquifer is also noted to contain occasional lamellae of carbonaceous clay (Andrews and Pearson, 1984) which would significantly increase expected U sorption. Use of a database more relevant for this material would lead, however, to overestimation of the retardation of U in the aquifer. This would be non-conservative from a safety assessment viewpoint and should thus be taken as an invalidation of this transport model with a performance assessment sorption database. As further back-up, an independent measurement of Kd on appropriate samples would thus be useful in this case to allow further model testing. Note also that the two points in Figure 2, at around 20 km down-gradient, which deviate markedly from the model predictions are from an area of irregular distribution of hydraulic conductivities (when compared to the rest of the modelled section of aquifer), indicating another area of weakness in this particular transport code.

The example above illustrates well several general limitations of such analogue studies. Firstly, data (e.g. Kd's) derived from curve fitting are always rather uncertain and agreement with independently evaluated values to within an order of magnitude or so should be considered to be quite reasonable. Secondly, performance assessment databases are generally selected to be conservative and this should be borne in mind in any comparison with field observations (i.e. the performance assessment model should overpredict migration). It is of note, however, that the seemingly excellent analogue validation of this particular transport model brought about no apparent change in the perceived robustness of the SWENT code. In fact, recent discussions with several of the workers involved in developing SWENT indicate that verification of the model against other transport codes was deemed to be more significant to increasing user confidence in the model. This begs the obvious and worrying question: what would have been the modellers reaction had the analogue study invalidated the SWENT code?

To date, such examples which can examine sections of a model for the purposes of validation are few. More frequently, studies of regional hydrology have been used in a semi-quantitative manner to indicate whether many of the implicit assumptions in transport models are valid. It is, for example, an unstated assumption in (all) transport models that the overall formation/aquifer chemistry will remain stable for the time period of concern. Studies of aquifer evolution suggest that this is probably not unreasonable in many cases (e.g. Edmunds et al., 1984; Zukin et al., 1987). However, large, relatively rapid changes (rather than evolution) in groundwater chemistry will clearly alter radionuclide migration processes in the groundwater via changes in solute speciation (and, therefore, sorption properties), bacterial populations, colloid formation (e.g. Gschwend and MacPharlane, 1990) and also, potentially drastic, changes in groundwater flow paths (e.g. Edmunds et al., 1988).

While measuring the natural decay series radionuclides in a sandstone aquifer, Cuttell et al. (1988) showed that major changes can occur in groundwater chemistry over a period of only ten thousand years. That the causes of the change, removal of original overburden and a drop in sea level due to glaciation, are recognised as cause for concern in several safety assessment studies (e.g. KBS, 1983) only serves to highlight the importance of the work.

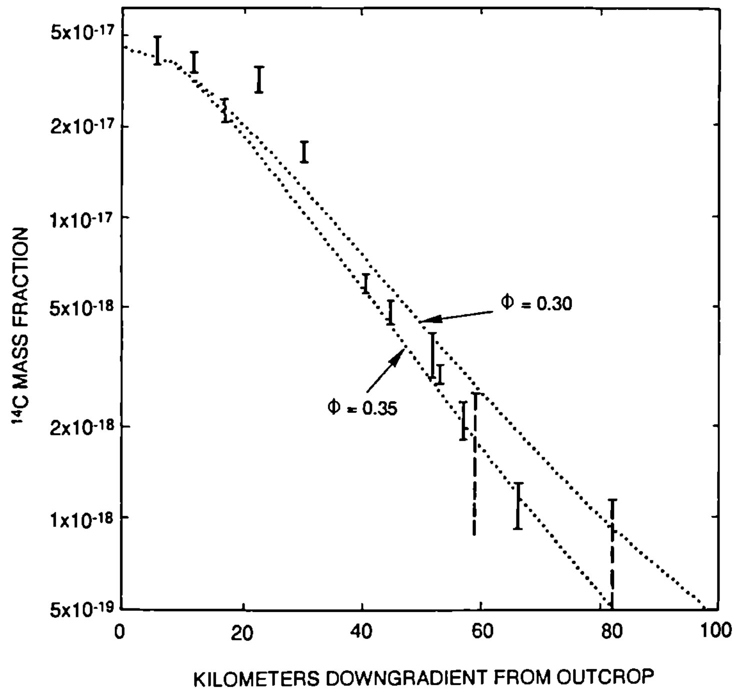

Figure 2: Measured and calculated C-14 contents with distance down-gradient from the outcrop (from Pearson et al., 1983). Note that the measured porosity (ϕ) in the aquifer section ranges between 0.30 and 0.40

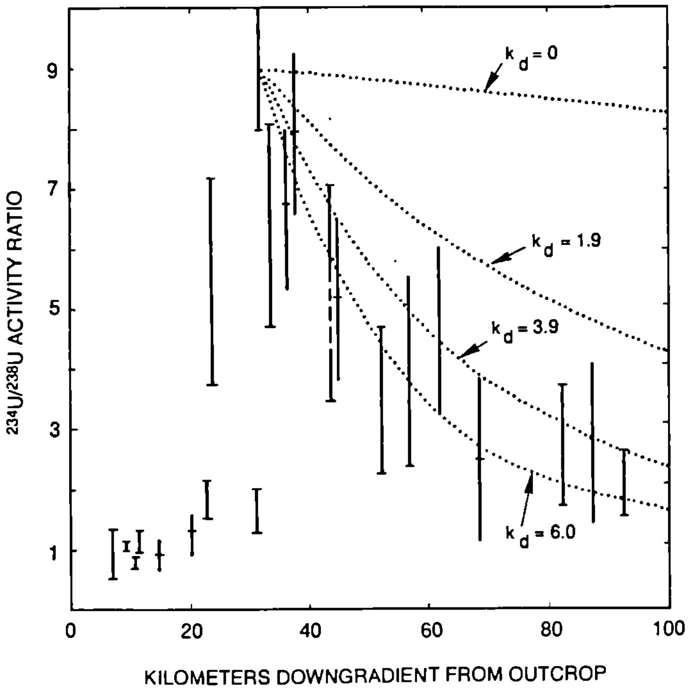

Figure 3: Measured and calculated uranium activity ratios with distance down-gradient from the outcrop (from Pearson et al., 1983). Note that Kd = 0 represents the case for the non-retarded C-14

This example may be viewed as merely a qualitative indication of the validity of certain transport models but the fact should not be overlooked that this study serves to indicate, quite clearly, that the assumption of invariant groundwater chemistry over long time periods, implicit in many transport models, is invalid under certain conditions. Thus even relatively simple studies of the natural environment, seeemingly unrelated to any specific aspect of any given transport model, can play a rôle in validification. Clearly such examples are of more relevance to those national programmes in which repositories will be sited in relatively shallow rock (e.g. Sweden, Finland).

Microscopic description of groundwater transport

It was stated above that, although geosphere transport models consider migration processes on a regional scale, the main mechanisms are, in fact, considered on a smaller, more manageable scale represented by the REV. Similarly then, although large-scale hydraulic models may be validated by regional studies, it is also necessary to examine many of the mechanisms of interest on a smaller scale. It may well be that a given geosphere transport model can be apparently validated on the basis of large-scale, regional studies but still contain numerous inconsistencies etc. in the representation of the REV. In a site characterisation much of this data would be collected, but often not in enough detail to allow a full definition of the REV (e.g. Nagra, 1988). Occasionally, a more detailed description of the physical aspects of a model REV may be produced for a specific experiment such as the radionuclide migration experiment in a simple fracture in granitic rock in the Grimsel Test Site (Meyer et al., 1989).

From the analogue viewpoint, however, little such work has been carried out. Alexander et al. (1990a,b) included a relatively superficial investigation of the microscopic details of fracture flow paths but this aspect of the studies was a secondary goal and led to no significant changes in the definition of the REV. More promisingly, a major study is presently underway which aims to study the physical aspects of a fracture flow path by a range of analytical methods (Heath, pers. comm.). It is planned to tie the physical description of the flow path to geochemical studies (of the form described in the next section) as a means of assessing the validity of the idealised fracture flow paths visualised in most REVs.

In the case of transport in porous media, it is assumed that dispersion (and advection) are constant, both spatially and temporally, at the scale of the REV. However, dispersion is generally defined at the scale of the pores in the given formation of interest even though dispersion in an aquifer is known to depend on heterogeneities of a much larger scale. In a recent study, Hoehn and Santschi (1987) describe a more precise definition of dispersion at the REV scale, obtained following a check on the consequences of the accidental release of 500 Ci of tritium into a river in northern Switzerland. The authors of this "semi-natural" analogue readily admit that the work was, in fact, carried out to monitor the accident "rather than to verify transport model assumptions" and that "this is often the case" in such studies. Once again, however, the significance of the data provided by this particular analogue appears to have been lost on most of the potential end-users (i.e. modellers). In discussions, the authors report only limited interest in the work, mainly by fellow field workers, and a reluctance by geosphere transport modellers to consider the implications of the study in any detail. This may well be a reflection of the (above noted) nature of this particular analogue but, while this may have reduced confidence in the data produced, it really should not be allowed to detract from the value of this parameter verification.

Retardation processes

Retardation of radionuclides migrating in groundwaters is represented in geosphere transport models by both physical retardation and chemical retardation. Consequently, these two major processes will also be separated here for simplicity.

The most important physical retardation processes can be classified as diffusion into secondary porosity, ion-exclusion and filtration. Generally, advective flow occurs in the primary connected porosity of the rock but nuclides may also diffuse into additional dead-end porosity. In a porous medium, this secondary porosity may be within the grains of the rock matrix and this process can be bulked into a sorption parameter. In any system containing small pores, nuclides may be excluded with resultant retardation due to filtration or ion-repulsion (as both the nuclides and the pore walls may be charged). Although these mechanisms depend on the physical characteristics of the flow system, they also depend to some extent on the radionuclide geochemistry (defining the size and charge of the dissolved radionuclide).

The form of matrix diffusion of most interest to geosphere transport modellers is that where advective flow in a rock formation occurs entirely in the fracture (or, in a sediment, primary) porosity while all solute transport in the bulk rock (or, in a sediment, secondary) porosity is diffusive (Neretnieks, 1980; Grisak and Pickens, 1980). Matrix diffusion is, potentially, of great importance in that it provides a mechanism which allows solutes access to the bulk rock, rather than just the fracture surfaces and any fracture-fill material present, so greatly enlarging the surface area of rock available for sorption processes. Non-sorbing radionuclides may also be diluted in the rock matrix. This could significantly increase radionuclide retardation in the far field and, when the resultant migration time is greater than the radionuclide half-life, decrease eventual releases by several orders of magnitude (KBS, 1983). The concentration maximum of long-lived, pulse-released radionuclides will also be reduced by the effects of temporal dilution (Nagra, 1985).

However, because the studies of Neretnieks (1980) and Grisak and Pickens (1980) were theoretically based, matrix diffusion had to be verified experimentally before the mechanism could be incorporated fully into transport codes. Two key parameters are required from any such study; the depth to which interconnected porosity could be shown to extend into the bulk rock (from the fracture/shear zone) and the diffusion rate of any given radionuclide in rock. It is interesting to note that, due to a lack of quantitative data at the time of their publication, two major predictive safety assessment studies produced in the last few years took up quite different stances on the extent of matrix diffusion. KBS (1983) assumed that a network of connected porosity extended throughout the entire rock (≈metres) while Nagra (1985) assumed that diffusion occurs only in dead-end pores or in a microfractured disturbed zone of very limited extent (≈mm) around the water conducting fractures (the limited matrix diffusion model of Hadermann and Roesel, 1985).

Clearly then the matrix diffusion concept required experimental verification. However, due to the very low diffusivities under consideration ($\approx 10^{-10}$ to 10^{-15} m^2s^{-1}), matrix diffusion is not very amenable to laboratory study. High diffusivity sandstones have been examined with some degree of success (Bradbury et al., 1986; Smith, 1990) but more relevant rock types such as granites and argillaceous rocks have proved much more problematic (e.g. Suksi et al, 1987; Ittner et al., 1988a,b). Major problems arise from sampling and preparation of the samples due to associated de-stressing of the rock, an inevitable consequences of removal to the laboratory, inducing non-reproducible changes to the pore geometry. Other perturbations due to sample cutting (as thin slices of 1 cm or so are usually studied) or grinding will also change both the pore geometry and the sorption properties of the rock. In general, all of the changes induced in the samples (see McKinley, 1989 for further details) tend to cause overestimation of the rock diffusivity, leading to an overestimation of matrix diffusion which is, in turn, non-conservative in the safety assessment sense as it leads to an apparently greater degree of radionuclide immobilisation in the far field.

Attempts have also been made to verify matrix diffusion by more complex experiments which, by confining the (larger) rock samples under high pressures (e.g. Brace et al., 1968; Bischoff et al., 1987; Drew and Vandergraaf, 1989) hoped to re-create the in-situ conditions more precisely. There are still many problems with such experiments: the low hydraulic conductivity means that unrealistically high pressure gradients have to be applied to the infiltrating fluids in order to produce breakthrough of radionuclides within reasonable time scales plus there is no way to guarantee that the re-established confining pressures will recreate anything like the original pore geometry. A, perhaps more telling, failure of such experiments is spelled out in a recent report by Smith et al. (1990). Here the authors applied the geosphere transport model RANCHMD to the data produced by infiltrating non-sorbing radiotracers through a fracture in a granitic core which was confined in a high-pressure cell (see Bischoff et al., 1987, for experimental details) and found that, due to the large number of undefinable experimental parameters, it was impossible to unambiguously de-couple matrix diffusion parameters from the experimental data.

Clearly then, accurate laboratory measurement of matrix diffusion and, subsequently, validation of transport models incorporating this concept are presently impossible (and will probably remain so). One approach which does, however, circumvent the problems indicated above involves the study of natural decay series radionuclides in profiles perpendicular to water-conducting fractures (Shea, 1984; Smellie and Stuckless, 1985; Smellie et al., 1986). The preferential mobility of U and Th daughters relative to their parents allows them to be mobilised from the bulk rock if connected porosity extends to an area of advective flow (in a nearby fracture, for example). The diffusion of such nuclides from the bulk rock into a fracture is thus analogous to the diffusion of a radionuclide (released from a repository) from the fracture into the rock as discussed in an earlier part of this section. Disequilibria in the natural decay series, indicating as it does preferential mobilisation of daughter nuclides due to rock-water reactions, can therefore indicate unequivocally the minimum depth of interconnected porosity in the rock adjacent to a fracture. Because of the clock provided by the decay process, such profiles may also provide indications of diffusion rates.

In a recent study utilising this technique, Alexander et al. (1990a) presented natural decay series data (Figure 4) for a rock core taken perpendicular to a water-conducting fracture in granitic rock. By means of detailed physical and geochemical characterisation of the core, along with the natural decay series results, it proved possible to verify that the observed Ra-226 profile was a result of rock-water interaction at depth in the rock followed by diffusion of the released Ra towards the fracture and immobilisation in the fracture fill material. This study is important from an analogue point of view for two main reasons. Firstly, the project was carried out on samples of the same fracture as were examined in the laboratory high-pressure infiltration experiment discussed in Smith et al. (1990). While the laboratory-based experiment produced ambiguous results when modelled, the analogue study of Alexander et al. (1990a) directly verified matrix diffusion (of at least a limited extent) in this rock-water system.

Furthermore, the analogue study also validated several of the important assumptions included in the RANCHMD code (although not the code in its entirety). It is asssumed within the code that a diffusion coefficient (Dp) of $1.5\mathrm{x}10^{-10}$ m^2s^{-1} will typify the rate of transport of most radionuclides in the zone of limited matrix diffusion. This is in excellent agreement with the range of 1.4 to $6.9\mathrm{x}10^{-10}$ m^2s^{-1} derived from the analogue study using the clock provided by the Ra-226 radioactive decay process (and agrees well with other published Ra diffusion rates; Sturchio et al., 1989). Thus, while a diffusion rate of 10^{-10} m^2s^{-1} in the zone of limited matrix diffusion was stated to be a conservative estimate in the Swiss safety assessment base case model (Nagra, 1985), it would appear to be reasonably realistic. It is also assumed in RANCHMD that the zone of influence of matrix diffusion is limited to only 0.001 m away from the fracture while the analogue study indicates that 0.01 to 0.05 m would be more appropriate. Altering the zone of unhindered matrix diffusion to 0.01 m, reduces the predicted peak concentration and increases break-through times of long-lived radionuclides by an order of magnitude when compared to the base case scenario. Thus, one of the main assumptions on the significance of matrix diffusion to radionuclide retention in the geosphere which is contained in the RANCHMD code can be seen to be potentially over-conservative in the safety assessment sense.

In fact, the results of other, similar studies of natural decay series disequilibria in the vicinity of water-bearing fractures in low diffusivity crystalline rocks (Smellie et al., 1986; Alexander et al, 1990b) suggest that the whole concept of limited matrix diffusion may be inappropriate at these locations. There is firm evidence that matrix diffusion is operating to distances of up to 0.2 m from some of the fractures described in these studies. In one core, from a hydrothermally weathered granite, diffusion may be significant to a depth of 0.5 m or more, supporting the KBS (1983) assumption of a network of connected porosity (with constant diffusivity) throughout the whole rock. Evidence from other studies of granitic rock appears to further substantiate this

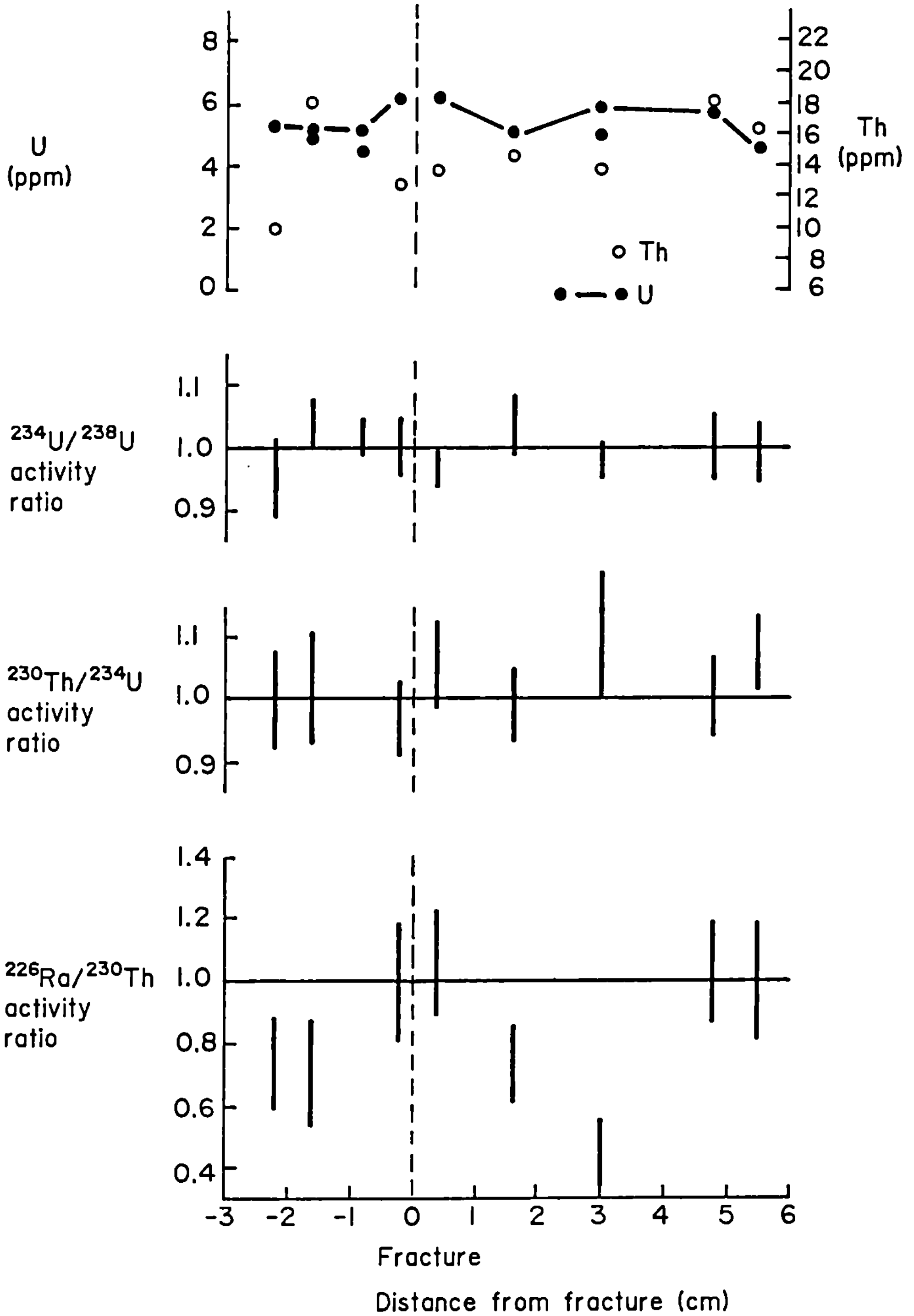

Figure 4: Natural decay series profiles perpendicular to a water conducting fracture, Grimsel Test Site, Switzerland. Assuming immobility of Th, the lowest profile displays preferential mobility of Ra-226 in the 0 to 4 cm and 0 to -3 cm zones around the fracture. Although the processes involved are unclear, this profile also indicates diffusion of Ra-226 from the rock towards the fracture over the last 1.6 to 8.0 x 10^3 years. Diffusion rates can thus be calculated using the observed interaction distance and the known time (from Ra-226 decay processes). Full details in Alexander et al. (1990a).

assumption. Jefferries (1987) reported the apparent diffusion of a suite of elements up to ≈1 m through a granite block immersed in seawater and Baertschi et al. (1990) describe the migration of U to depths of 0.8 m through an aplitic granite in the tunnels of Nagra's Grimsel Test Site. In both cases the driving force was, in fact, shown to be predominantly capillary flow, due to drying out of the granite block before seawater immersion in the former study and due to drying of the tunnel walls by forced ventilation in the latter. The studies nevertheless clearly show the presence of connected porosity.

The study of matrix diffusion in sediments has received little or no attention to date although a small, pilot study (Mazurek, 1990) on matrix diffusion in the vicinity of a water conducting fracture in a claystone (the Opalinus Clay of Central Europe) shows evidence of diffusion driven processes effecting the bulk rock up to several centimetres from the fracture.

In an argillaceous rock repository, it is likely that little or no advective flow of groundwaters would occur, either because the host formation is highly impermeable or isolated from the regional groundwater flow regime by aquitards (Opalinus Clay, Swiss HLW; Boom Clay, Belgian HLW). In this case, transport is assumed to occur predominantly by diffusion (as is transport through the bentonite backfill of the Swedish and Swiss HLW repositories).

Some laboratory data does, in this case, exist on diffusion rates in clays. Most experiments are, however, of short duration and are relatively crude, utilising confinement methods which perturb the samples (e.g. Bradbury et al., 1986; Berry et al., 1988) and pore solutions which are not representative of in-situ conditions (e.g. Czurda et al., 1987; Wagner, 1988). Direct analogue evidence is required of long-term diffusion in clays to validate the laboratory experiments (and thus the safety assessment predictions). Several analogue examples of migration in clays exist (e.g. Colley et al., 1984; Colley and Thomson, 1985; Hofmann, 1990) but a particularly good example is that of Loch Lomond, West Scotland (MacKenzie et al., 1983, 1984, 1990; Hooker et al., 1985). The sediment of this freshwater loch contains an ≈1 m thick band of marine sediment, some 4 m below the present loch bed, which was deposited during the Flandrian transgression some 5000 years ago (see Figure 5). Following a subsequent sea-level regression, the marine band was buried below later freshwater sediments and the marine sediment and associated porewaters, being of significantly different composition, therefore formed a geochemical discontinuity which acted as a subsequent source term for the migration of a range of elements into the surrounding (freshwater) clays. This migration is thus analogous to that of radionuclides transported through argillaceous rocks (or that released from the waste matrix and container, into a clay backfill). On the basis of several reasonable assumptions (e.g. porosity, sorption coefficients, timescales), the observed mobility of a range of elements was shown to be compatible with the safety assessment model predictions (based on laboratory data) although the halogens I and Br were, in fact, much less mobile than predicted. The calculated diffusion rate (De) for Br of 10^{-11} m^2s^{-1} was approximately an order of magnitude lower than predicted from laboratory experiments, suggesting that the safety assessment models were, therefore, over-conservative in their assumptions of migration rates in the clay backfill of the repository near field.

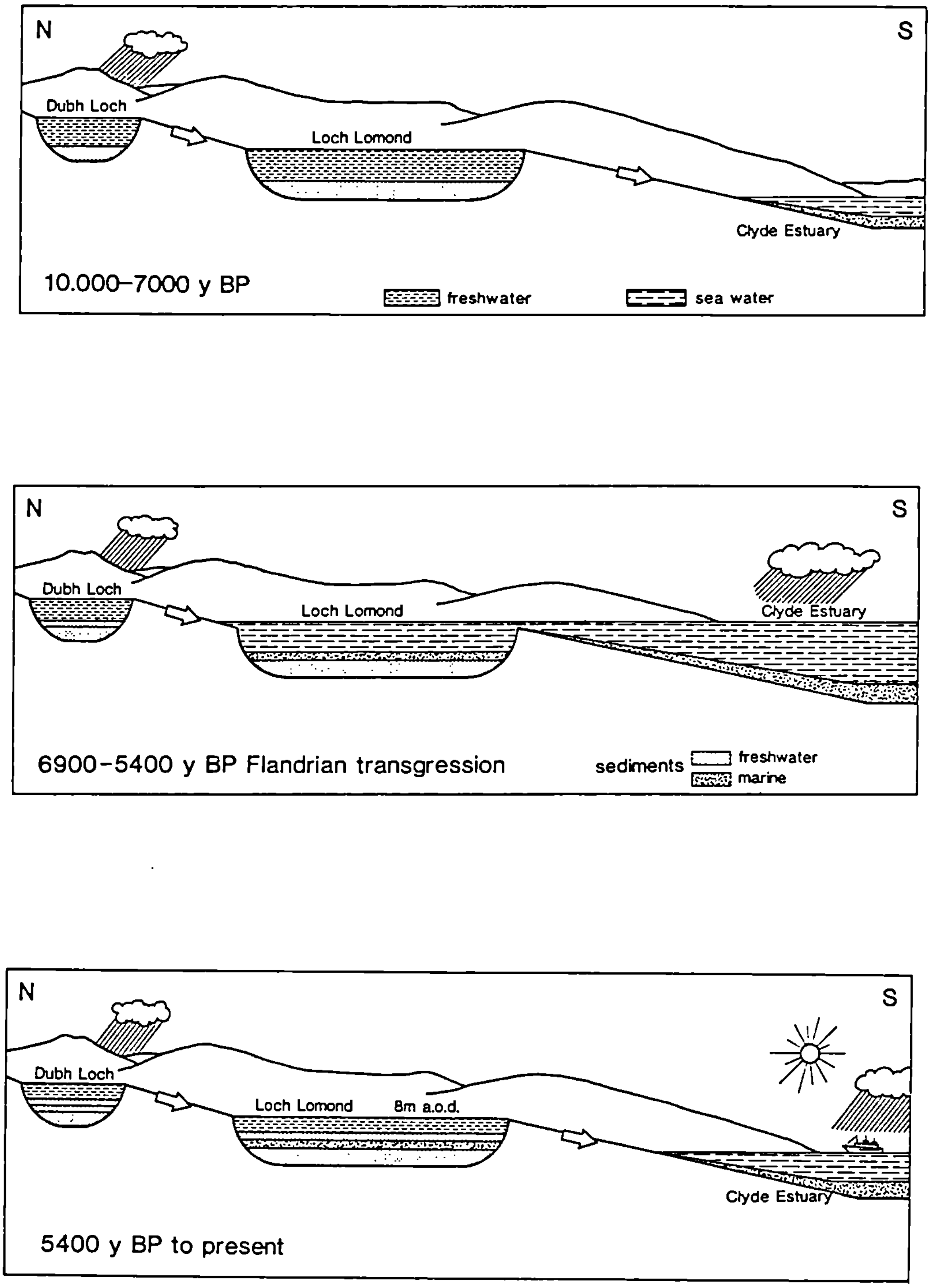

Figure 5: Schematic representation of the deposition of the marine band in the freshwater Loch Lomond, West Scotland

It should, however, not be forgotten that, although the loch sediment column was extremely well characterised (both physically and chemically), the boundary conditions were still very difficult to define precisely. Assumptions were made that:

1 The physico-chemical conditions in the sediments remained constant for over 5000 years, including constant sedimentation rates (this was supported by evidence on sedimentation rates from C-14, Cs-137 and Pb-210)

2 There was no significant advective transport (e.g. wave stirring, bioturbation) during this time other than that due to compaction of the sediment column

3 The initial concentrations of the elements and species of interest had to be assumed

4 The form of the Br in the marine band had to be estimated. It was established to be closely correlated with the organic content of the core.

To be fair, most of these assumptions are not unreasonable in that a large body of data exists in the marine and lacustrine literature which could be extrapolated to the Loch Lomond situation quite readily.

It has been suggested that this study, because of the above assumptions, can be quoted as being no more than a semi-quantitative validation of the models in question. However, examination of the data indicates that the largest uncertainty in the calculated diffusion rate for Br was the assumed initial concentration of Br in the marine sediment band. Varying the Br concentration between 20 ppm and 60 ppm produced a range in De of 3 to 8 x 10^{-11} m^2s^{-1}. When this range is compared with laboratory-based experimental results of anionic diffusion in clays, where the range may cover an order of magnitude or more for a given experiment (e.g. Albinsson and Engkvist, 1989, Albinsson et al., 1990), it is clear that the values are neither better nor worse than a laboratory-based experiment, indicating that this analogue validation study is as quantitative as any that can be produced by laboratory experiments.

In the preceding examples of diffusive transport, it is assumed that transport occurs at the ambient host rock temperature. In some national programmes, however, it is planned to place heat-omitting waste at high density in deep repositories with a subsequent large increase in temperature in the host rock around the engineered barriers. Consequently, studies in France and the USA (mainly) have included the examination of transport properties during hydrothermal alteration, usually associated with U-ore emplacement (e.g. Shea, 1984; Cathelineau and Vergneaud, 1989; Ménager et al., 1990) or other hydrothermal systems (e.g. Cathelineau, 1987; Alexander et al., 1988) and the hydrothermally/thermally altered contact zones around igneous intrusions (e.g. Brookins et al., 1981; Brookins, 1986; Wollenberg and Flexser, 1986). The best known study is, of course, that of the Oklo natural reactors in the Gabon, West Africa, where major hydrothermal circulation resulted from reactor operation and caused some redistribution of fission/activation products (De Laeter et al., 1980; Brookins, 1983; Jakubick and Church, 1986).

The results of these studies are encouraging in that many elements of interest show little or no migration. U and the REE (chemical analogues of the actinides) appear to be advectively transported over only a few metres or less (Wollenberg and Flexser, 1986; Ménager et al., 1990) or to have undergone only diffusive transport (Shea, 1984). The work of Curtis et al. (1989) at Oklo is perhaps even more useful in that several important elements are seen to migrate significant distances and are therefore now known to be worthy of further study.

Overall, however, all of the above studies are no more than qualitative demonstrations of radionuclide migration behaviour in the perturbed zone around a repository. The source term is frequently difficult to define, as are the precise physico-chemical conditions at the time of element migration (or retardation). The volume of fluid circulated through most hydrothermal systems studied is much greater than that expected to pass through the near-field and near-field/far-field interface during the period of elevated repository temperatures and the fluid compositions are also atypical. Much more important: the hydrothermally induced migration or retention of elements is actually of no direct relevance to a repository predictive safety assessement study. Apart from a few scenarios in which early failure of canisters occurs and the backfill causes little retention (e.g. US Yucca Mountain concept) no release of radionuclides from the near field is expected until well after the period of higher temperatures has passed. Also, it is unlikely that temperatures in the host rock will be much higher than 100°C, whereas the temperatures calculated in the studies quoted above ranged from 250 to 650°C. At those temperatures even Th is mobilised (Langmuir and Herman, 1980) and the REE geochemistry becomes complicated (Humphris, 1984). There is, of course, a period during any hydrothermal event when the temperature decreases and may well drop below 100°C (depending on the formation ambient temperature), but trying to disentangle the subsequent lower temperature overprint from the higher temperature mobilisation is a fearsome task (ask any metamorphic petrologist or geochemist) and is unlikely to provide enough unambiguous data to be of use for a geosphere transport model.

To summarise, such studies as carried out to date on hydrothermal or intrusive systems in igneous rock, while providing little data of relevance to the migration of radionuclides in the thermally affected near-field/far-field interface, are useful in that they, encouragingly, display only limited migration of many elements of interest to safety assessment. It may be more appropriate in the future if detailed mineralogical and structural studies of low-temperature ($\approx$100°C) hydrothermally altered zones are carried out (along the lines of, for example, Ménager et al., 1990). This will allow a more concise definition of the secondary mineralogy to be expected in the thermally perturbed zone of the repository host formation which can then be used to direct (laboratory or analogue based) sorption studies with the relevant mineralogy and radionuclides. Obviously, an analogue study which could combine these two (i.e. initial, low temperature hydrothermal alteration of an igneous rock followed by infiltration of, for example, uraniferous groundwaters) would be the ideal case.

A final physical retardation mechanism which is intrinsically suited to analogue study is that of filtration of groundwater colloids (and particles) in the natural groundwater system. The use of bentonite as the back-fill in a HLW repository should prevent the escape of colloids from the near-field but cannot stop the later formation of radiocolloids when radionuclides in solution (in the far-field) become associated with natural colloids in the groundwater. The radiocolloids could then enhance doses to the biosphere by moving through the far field with minimal retardation (assuming no sorption on the rock nor filtration by fracture infill material or in pore spaces (Avogadro and de Marsily, 1984). Numerous field experiments have indicated that artificial colloids, bacteria and viruses can be transported significant distances in aquifers (e.g. Keswick et al., 1982; McCarthy and Zachara, 1989; Penrose et al., 1990). Laboratory-based experimental study of such systems have also been reported (e.g. Eichholz et al., 1982; Saltelli et al., 1984) but, as with the matrix diffusion studies, the results are of no use for model validation due to the poorly controlled nature of the experiment allied to the fact that the laboratory-based studies are non-representative of the natural flow systems.

The great advantage of an analogue evaluation of colloid transport is that, by employing tracers naturally present in the colloid/rock/groundwater systems, there are no experimental artefacts: the colloid size distribution and composition, for example, are obviously completely representative of the natural system, something which cannot be claimed for a colloid migration experiment which employs artificial or treated materials. There have been, however, very few analogue studies of natural colloid migration in appropriate systems. Ivanovich et al. (1988), for example, reported the presence of U in association with colloidal clays in a schist groundwater. Although this work was carried out as part of the Alligator Rivers Analogue (ARA) Project, it is of note that the rôle of colloids in solute transport has been specifically omitted from the ARA project geosphere transport model currently under development (Lever et al., 1989). Colloids have also been shown to be an important reservoir for many natural radionuclides and trace elements in the Poços de Caldas study, but there is little evidence that such colloids are mobile in this system (Miekeley et al., 1990).

Although the filtration of colloids is also not included in current Swiss geosphere transport codes, investigations have been carried out to validate this aspect of the model. Hofmann (1989) reported the apparent transport of colloids in the (open) fracture system of the Bärhalde granite of the southern Black Forest, FRG, and a more detailed follow up (Alexander et al., 1990c) has indicated the need for further work on the problem. The data of Hofmann (1989) suggested that natural (clay) colloids were being transported up to 5 km, in sub-surface fracture systems, from a local topographic high (the Feldberg gneiss) to the Krunkelbach mine in the neighbouring Bärhalde granite. New data (Figure 6) strengthens the original work of Hofmann (1989), with the colloid REE signature significantly different to that of the granite in which they were collected but similar to that of the neighbouring gneiss.

This study in no way invalidates the current generation of Swiss geosphere transport models as the data is, as yet, only tentative (only four samples were collected before the mine was closed), but it does indicate the possibilities of such a study of the natural groundwater system.

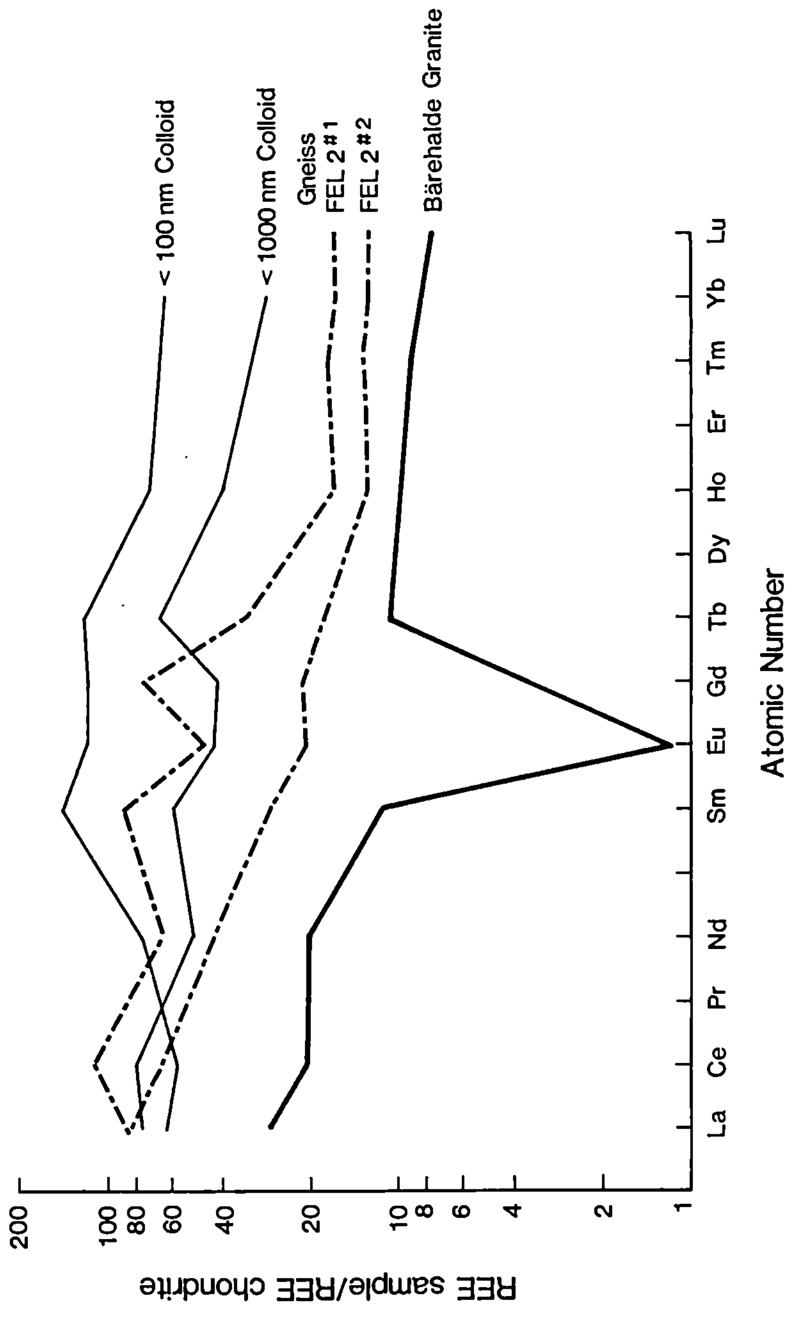

Figure 6: Chondrite normalised REE plot for the phases of interest in the Black Forest colloid transport study (from Alexander et al., 1990c). FEL2 represents the gneiss from the zone of groundwater infiltration and this is significantly different from that of the Bärhalde granite (the mine host formation and groundwater sampling site). Note that the REE signature of the colloids filtered from the granite groundwater is similar to that of the gneiss formation, some 5 km distant from the mine in the granite, and is unlike that of the granite.

Most geosphere transport models incorporate a simple definition of sorption processes, usually in the form of a distribution coefficient or Kd value, to describe radionuclide retardation in the far-field due to sorption (equation 4 being of the most common type). Occasionally, the limitations in the sorption database are clearly stated and the Kd values used carefully chosen to ensure conservative over-prediction of migration (by the transport model), even when the simple Kd concept is known to be invalid (e.g. McKinley and Hadermann, 1984), but the direct use of batch sorption derived Kd values is generally difficult to justify (see discussions in Bradbury and Jeffries, 1985, and Bradbury et al., 1990, for example). Arguably, the further development of transport models which take into account non-linear sorption (equation 5) will produce more valid descriptions of radionuclide migration in the far field. These non-linear sorption models, such as Jakob et al. (1990), still, nevertheless, depend on laboratory-based data and the question of validity of such an approach will remain.

One possible way round this would be to validate geosphere transport models by analogue studies. Here the connection between measured values and the far field environment is much clearer than, for example, batch or column sorption experiments carried out on crushed rock on laboratory bench tops. One approach which has gained in popularity recently is that of measuring Kd values directly in the natural environment - the so-called in-situ Kd technique. Unfortunately, the definition of Kd is, in fact, extremeley confused and, consequently, much of the data resulting from the numerous "in-situ Kd" analogues is no more useful than laboratory-based Kd measurements and may be highly non-conservative in a safety assessment sense (McKinley and Alexander, 1990).

The main problems arise due to a misinterpretation of the Kd definition and it is, therefore, useful to re-iterate the generally accepted constraints here. As was mentioned in equation 4,

$$C_R = KdC_w$$

While for some simple systems (e.g. pure ion exchangers) such a defined Kd may be thermodynamically based, the value input to geosphere transport models is usually a (more or less) empirical representation of kinetically fast, concentration independent, reversible sorption. Several other points require clarification too. According to McKinley and Alexander (1990), the Kd concept is constrained in that

a) Solute reactions occur only with those rock surfaces in contact with connected, saturated porosity and so the bulk rock may be of limited importance (when it is not in contact with the solute)

b) The number of sites on any given solid phase which are available for sorption is limited and, when these are filled, there is no relationship between solution and solid phase concentrations (c.f. Figure 1)

c) Precipitation (of any form) must not be included with sorption in a Kd-type distribution coefficient, i.e. in this case there is no connection between the bulk rock or precipitate concentration and the solution concentration.

This then defines sorption in the far field as any process which distributes a species between the groundwater and the rock in such a manner that the equilibrium rock concentration is functionally related directly to the (equilibrium) groundwater concentration.

This is, in fact, demanding rather a lot from any analogue but it is of note that, in most laboratory batch sorption experiments (where the redistribution of a tracer between rock and a solution is measured (see Sibley and Myttenaere, 1986, for a review), the measured partitioning of the solute is not proven to be kinetically fast, concentration-independent and reversible.

Several reports have thus stated that a better way to evalutate Kd's is to do so in the natural environment, usually by simply measuring the concentrations of naturally occuring radionuclides in a rock and its associated ground(pore)water. As is clear from the preceding comments, however, this is only true, and therefore only of relevance to geosphere transport models, when it can be shown that the solid-phase measurements reflect only material which is exchangeable with solution and when the entire rock-water system is in equilibrium. This point is rarely addressed in most studies and here a few examples will be discussed to indicate the problems associated with the entire in-situ Kd concept and its irrelevance to geosphere transport systems. Much of what follows summarises McKinley and Alexander (1990) and a wider ranging discussion may be found therein.

One method of deriving in-situ Kd values is from concentration profiles of the sort displayed in Figure 4. Here a well defined (and dated) geochemical anomalogy is defined in terms of a retardation factor, if the water velocity is known. In the study of Alexander et al. (1990a), a curve was fitted to the observed diffusion profile and a Kd extracted. The problem, however, with this and similar studies is that, while the value may adequately represent the oberved data, there is no guarantee that the derived Kd is applicable outside the actual system studied.

The in-situ Kd concept is being applied rather extensively in the ARA project (Duerden, 1989, 1990). Here the investigators attempt to define those phases actually involved in sorption processes and, hopefully, so attain an in-situ Kd value which avoids including non-available solid-phase elements held in the rock matrix. This approach is encouraging in that, in theory at least, it should produce more accurate data (although it may still be regarded as non-conservative from the safety assessment viewpoint). Problems arise, however, from the fact that phase definition is produced by selective chemical leachants, using many of the numerous methods available in the literature. Leaching schemes such as these produce no more than operationally defined partition of elements between the various fraction of the rock and it is rarely evident that discrete phases associated with each fraction actually exist in any given sample. Most leachants are, in fact, highly non-specific (see Martin et al., 1987, for example) and the potential re-adsorption of trace elements, released by a leachant, back onto the solid phase is also well documented (e.g. Sholkovitz, 1989).

Some attempts have been made to answer these criticisms by physical examination of the rock phases after each leach (Nightingale, 1988) and further work is planned in the ARA project (Duerden, 1990) but any Kd's so produced to date should be regarded with extreme caution.

Probably the most common method for deriving in-situ Kd's is based on the work of Krishnaswami et al. (1982) and has been repeated extensively (e.g. Laul et al., 1985, 1986; Ivanovich et al., 1988). In effect, the method measures natural decay series disequilibria in natural waters and proceeds from the key equations

$$P + K_2C^- = \lambda C + K_1C \text{ (solution phase)} \tag{7}$$

and

$$K_1C = \lambda C^- + K_2C^- \text{ (solid phase)} \tag{8}$$

where

P = supply rate of nuclide to solution by dissolution, in-situ production and recoil (atoms time^{-1} vol. of water^{-1})

λ = radioactive decay constant of the nuclide (time^{-1})

C = concentration of nuclide in water (atoms vol. of water^{-1})

C^- = concentration of nuclide absorbed on surfaces (atoms vol. water^{-1})

K_1 and K_2 as defined before.

These equations were defined for steady state conditions in a closed aquifer. It is also of note that the solution production rate (P) allows for input by dissolution and recoil but that removal from solution is only by decay and sorption. This is probably inapplicable in most potential repository host formations as, due to the desired low groundwater flow rates, loss by precipitation/ co-precipitation may be significant. Further, equation (8) is correct for the sorbed phase only when no radionuclide is produced directly in a sorbed phase by processes such as solution-solid or solid-solid recoil.

Assuming that all the sorption processes can be described, as in equation (4), as a simple Kd, equation (8) becomes

$$R = \frac{K_1 + K_2 + \lambda}{K_2 + \lambda} \tag{9}$$

where R is the retardation factor

Clearly then, this states that for all isotopes of a given element e.g. U) the retardation factor (and thus Kd) would be dependent on the half-life of the radionuclide. Such decay-dependent in-situ Kd's (and R's) are not compatable with conventionally defined Kd's (Ivanovich et al., 1990) and most of the above assumptions are questionable on other grounds (McKinley and Alexander, 1990).

It is also highly debatable whether the effective use of Rn-222 and Ra-226 as ideal reference isotopic tracer, inherent to all of the above mentioned studies (and Laul and Smith, 1988; Dearlove et al., 1989) is justified from considerations of the Rn-222 decay process of the former as discussed elsewhere (e.g. Rama and Moore, 1984; Cuttell et al., 1988; Ivanovich et al., 1990) and the sorption and solubility limits of the latter (e.g. Langmuir and Melchior, 1985).

In summary then, the claims made for in-situ Kd values generally seem based on a poor understanding of sorption phenomena and the definition of distribution coefficents or Kd's. Thus the statement of Laul et al. (1985) that "These in-situ Kd's are true site specific values that can be used in transport modelling" is clearly incorrect. In this study, the measured values apply only to a single element concentration and, without knowledge of the sorption isotherm, can in no way whatsoever be extrapolated to safety- relevant concentrations for insertion into a geosphere transport model.

One other topic worth mentioning is that of redox processes. In both the Nagra (1985) and KBS (1983) predictive performance assessments, a redox front is assumed to exist in the near field (plus, perhaps to penetrate the near-field/far-field interface) and, in principle, to also exist as a further migration barrier at the reducing deep groundwater/oxic shallow groundwater boundary. A significant amount of information exists on the retardation of elements in the vicinity of redox fronts, with U roll-fronts (e.g. Cheney and Trammell, 1973; Brookins, 1987; Deutsch and Serne, 1984), reduction haloes (see the review of Hofmann, 1990) and marine redox diagenesis (e.g. Aller, 1980; Colley and Thomson, 1985) in particular described extensively. To date, most modelling work has concentrated on describing changes in solute speciation associated with such fronts (see the review of Read and Hooker, 1990) but it should not be forgotten that elemental sorption of Fe-oxyhydroxides also occurs and may then be amenable to a simple retardation coefficient description.

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

This review has shown that the value of analogues in testing or validating models of rdionuclide transport is widely recognised and many studies have been carried out with this aim in mind. In general, however, such studies have tended to be rather poorly focussed with little relevance to the models used in performance assessment. In some cases, indeed, due to confusion of terminology, the conclusions drawn can be incorrect or misleading.

The most useful studies to date have been those which focussed on determining the existence and scale of a particular process (e.g. matrix diffusion) or examined transport in very simple hydraulic systems (e.g. large aquifers, clays where diffusive transport dominates). In these cases, some very clear conclusions can be drawn but there is little evidence that these results are acknowledged by the performance assessment community and used to improve their models. This is partly due to the attitude of many modellers, considering that such an unconstrained, poorly understood system as the natural environment cannot possibly provide the hard data necessary to verify and validate transport models. Blame must, however, also be shared by the analogue community in that it is clear that the full value and true significance of many studies are not properly communicated to the end-users (the modellers).

It may be concluded that, despite its acknowledged importance, this is an area in which input from the modellers is still weak and in which the useful output poorly represents the investment in terms of finance and manpower.

In order to improve matters, it is recommended that:

a) Research proposals and papers on this topic are carefully reviewed for relevance. Eliminating the many purely academic studies which are tied to the nuclear waste bandwagon would help greatly to improve the standard of such studies

b) Direct input from the performance assessment modellers is incorporated at both planning and interpretative stages of these studies

c) Work is focussed on environments of key relevance for performance assessment - e.g. low flow, chemically reducing, fissure flow system, etc.

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NATURAL ANALOGS AND PERFORMANCE ASSESSMENT OF THE GEOLOGICAL DISPOSAL OF NUCLEAR WASTE : A REVIEW

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Extended summary

The objective of this invited paper was to review the use of natural analogs in supporting the performance assessment of the safety of geological disposal of nuclear waste. The impact of legislation passed in Sweden and Switzerland was discussed. For example, the Swedish Stipulation Act of April , 1977, in part stated, "permission to fuel reactors to be granted only if the owner has demonstrated how and where absolutely safe final disposal can be effected". This led to the utilities starting the KBS projects and the major KBS reports were used successfully to support their applications for fueling licences. Similarly, the Swiss Federal government ruling in October, 1978, required "permanent, safe management and final disposal of radioactive waste as a prerequisite to future development of nuclear energy". Futhermore, the Swiss Federal Department of Transport, Communication and Energy required that a project be initiated to offer a guarantee of feasible, safe final disposal as a prerequisite to renewing power reactor operational licences beyond 1985. This led to the Project Gewahr report, submitted to the Swiss Federal government in 1985, and conditionally accepted in 1988. These laws and the utilities' response in Sweden and Switzerland have had a major impact on waste management and, in particular, on natural analogs. The requirement to guarantee the absolute safety of geologic disposal in the absence of detailed site-specific information led to a major emphasis on massive engineered barriers such as thick copper or steel containers, massive bentonite clay seals, and concrete bulkheads. Hence, the emphasis of natural analog programs has been to support the performance assessment of these engineered barriers and to ensure the important near-field chemical and physical processes were well understood. Progress was outlined by means of illustrative examples from a number of national and international programs.

The major performance assessments conducted in the past ten years were summarized and the differences between disposing of spent fuel and vitrified reprocessing waste were outlined. In most of these assessments, the very long containment of radioactivity is done by the geologic formation. It was pointed out that comparing different disposal concepts in different geologies can reasonably only be done with site-specific geological data.

The overall conclusion of this review paper was that most of the natural analog studies have supported near-field models of performance assessment. There are few examples of far-field applications. Futhermore, it was concluded that acquiring information on natural systems to support performance assessment models of the far-field should be an important part of a site characterization plan since many of the

processes are geology specific and some are site specific. Examples of how this might be done were given with emphasis on the AECL field programs at Whiteshell, Manitoba and Atikokan, Ontario in Canada. The detailed geological description of a site should include an explanation or history of its geological/geochemical development. In the case of granitic intrusives, the rock mass has been subjected to a number of physical and chemical events whose effects are recorded for example, in the present geometry and geochemical character of the fractures.

The concept of negative analogs was discussed. It was emphasized that it is equally important to understand both those observations of natural systems that support performance assessment and those that apparently invalidate it. The need to understand the processes occurring in these 'negative analogs' was illustrated by discussing examples such as the massive degradation of granite by kaolinization, and the formation of uranium ore deposits requiring a massive movement of uranium.

Note :

"The Canadian Nuclear Fuel Waste Management program is jointly funded by AECL and Ontario Hydro under the auspices of the CANDU Owners Group".

APPENDIX 1

Abstracts of Poços de Caldas project reports
(draft versions)

Poços de Caldas Project Final Workshop

Introduction to the Papers

The Poços de Caldas Project was designed to study processes occurring in a natural environment which contains many features of significance to the safety assessment of radioactive waste disposal. The study area, in the province of Minas Gerais, Brazil, is a region of high natural radioactivity associated with volcanic rocks, geothermal springs, and uranium ore deposits. It contains two sites of particular interest, on which the project work was focussed: the Osamu Utsumi uranium mine, and the Morro do Ferro thorium/rare-earth ore body. The first site is notable, in particular, for the prominent redox fronts contained in the rock, while Morro do Ferro was already well known as one of the most naturally radioactive locations on the surface of the Earth, owing to the high thorium ore grade and the shallow, localised nature of the deposit.

The features displayed by these two sites presented the opportunity to study a number of issues of concern in repository performance assessment, in particular the studies could:

- assist in the validation of equilibrium thermodynamic codes and databases used to evaluate rock/water interactions and the solubility/speciation of elements

- determine the interactions of natural groundwater colloids, radionuclides, and mineral surfaces with respect to radionuclide transport processes and colloid stability

- produce a model of the geochemical evolution of redox fronts, specifically aimed at understanding long-term, large-scale movements of redox-sensitive natural series radionuclides (including, if possible, natural Pu and Tc)

- model the migration of REE/U-Th series radionuclides during hydrothermal activity similar to that anticipated in the very near-field of some spent-fuel repositories.

The project ran for three and a half years from June 1986 until December 1989 under the joint sponsorship of SKB (Sweden), NAGRA (Switzerland), the Department of the Environment (UK) and the Department of Energy (USA), with considerable support from a number of organisations in Brazil, notably Nuclebras (now Uranio do Brasil). The first year feasibility study was followed by 2.5 years of data collection and interpretation.

The fourth CEC NAWG was seen as a very appropriate venue for presenting the end-of-project results from Poços de Caldas, and allowing wider discussion of the findings. Draft versions of the fifteen technical reports stemming from the Project were on view at the meeting, and will be published by the funding bodies later this year. A very wide range of data and material is available from the two sites studied, and further interpretation beyond the end-of-project results presented here is clearly possible, and will undoubtedly take place in coming years. The project sponsors encourage the widest possible use of the information by other interested parties, and copies of the reports are available to such groups.

In this NAWG Summary Report only the abstracts of the 14 data reports are presented, to give a flavour of the scope of the project. The final Summary Report of the Project (No. 15 in the Series; listed below) brings this information and interpretation together to give a complete overview, and is available from the funding organisations.

Poços de Caldas Project Report Series

Series A: Data, Descriptive, Interpretation

Report No.	Topic	Authors (Lead in Capitals)
1.	Outline of regional geology, mineralogy and geochemistry, Poços de Caldas, Minas Gerais, Brazil.	SCHORSCHER, Shea.
2.	Mineralogy, petrology and geochemistry of the Poços de Caldas analogue study sites, Minas Gerais, Brazil. I: Osamu Utsumi uranium mine.	WABER, Schorscher, MacKenzie, Peters.
3.	Mineralogy, petrology and geochemistry of the Poços de Caldas analogue study sites, Minas Gerais, Brazil. II: Morro do Ferro.	WABER.
4.	Isotopic geochemical characterisation of selected nepheline syenites and phonolites from the Poços de Caldas alkaline complex, Minas Gerais, Brazil.	SHEA.
5.	Geomorphological and hydrogeological features of the Poços de Caldas caldera, and the Osamu Utsumi mine and Morro do Ferro analogue study sites, Brazil.	HOLMES, Pitty, Noy.
6.	Chemical and isotopic composition of groundwaters and their seasonal variability at the Osamu Utsumi and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.	NORDSTROM, Smellie, Wolf.
7.	Natural radionuclide and stable element studies of rock samples from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.	MacKENZIE, Linsalata, Miekely, Scott, Osmond, Curtis.
8.	Natural series nuclide and rare earth element geochemistry of waters from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.	MIEKELEY, Coutinho de Jesus, Porto da Silveira, Linsalata, Andrews, Osmond.
9.	Chemical and physical characterisation of suspended particles and colloids in waters from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.	MIEKELEY, Coutinho de Jesus, Porto da Silveira, Degueldre.
10.	Microbiological analysis at the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.	WEST, Vialta, McKinley.

Series B: Predictive Modelling and Performance Assessment Group

11.	Testing of geochemical models in the Poços de Caldas analogue study.	BRUNO, Cross, Eikenberg, McKinley, Read, Sandino, Sellin.
12.	Testing models of redox front migration and geochemistry at the Osamu Utsumi mine and Morro do Ferro analogue sites, Poços de Caldas, Brazil.	Ed: McKINLEY, Cross, Haworth, Lichtner, MacKenzie, Moreno, Neretnieks, Nordstrom, Read, Romero, Scott, Sharland, Tweed.
13.	Near-field high temperature transport: Evidence from the genesis of the Osamu Utsumi uranium mine analogue site, Poços de Caldas, Brazil.	CATHLES, Shea.
14.	Geochemical modelling of water-rock interactions at the Osamu Utsumi mine and Morro do Ferro analogue sites, Poços de Caldas, Brazil.	NORDSTROM, Puigdomènech, McNutt.

Summary Report

15.	The Poços de Caldas Project: Summary and implications for radioactive waste management.	CHAPMAN, McKinley, Shea, Smellie.

The regional geology, mineralogy and geochemistry of the Poços de Caldas alkaline caldera complex, Minas Gerais, Brazil.

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Abstract

The Poços de Caldas Alkaline Complex, the largest in South America, is circular-shaped with a mean diameter of about 33 km. It is one of the Mesozoic alkaline occurrences of South Eastern Brazil that developed from the Upper Jurassic onwards, during continental break-up and drift. It comprises a suite of alkaline volcanic and plutonic rocks (mainly phonolites and nepheline syenites) with a normal lack of background amounts of U, Th and rare earth elements (REE). The evolutionary history began with a major early volcanism involving ankaratrites and phonolite lavas, and volcanoclastics, followed by caldera subsidence and nepheline syenite intrusions forming minor ring dykes, various intrusive bodies, and circular structures. Finally, strongly incompatible elements led to the formation of the enriched eudialyte nepheline syenites and phonolites.

The magmatic evolution included deuteric processes indicating a volatile rich parent magma. These processes extended over a large temperature range and resulted in the formation of pegmatitic veins, of pneumatolitic and auto-hydrothermal mineralizations (including rare metal silicates such as giannettite),various zeolites, fluorite, and hematite, together with mineral alterations. These alterations developed from magmatic pseudoleucite formation through alkali-exchange reactions to a "clouding" of the main alkali feldspars under auto-hydrothermal conditions (with fluid inclusion formation, incipient kaolinization, and hematite-hydrous ferric oxide pigmentation). Geochemically, the resulting rocks are enriched mainly in potassium when compared to global nepheline syenites and phonolites. Mobilization and concentration of U, Th and REE at this stage could not be detected.

At least at one place (Morro do Ferro) the intermediate nepheline suite was affected by a carbonatite intrusion and the formation of a stockwork of magnetite veins.

Very intensive hydrothermal K- and S-rich alteration associated with penecontemporaneous formation of magmatic breccias, occurred locally.

These processes led to the formation of several important radioactive and REE-rich anomalies. Two of these: the Th-REE occurrence of Morro do Ferro and the U-Zr-REE occurrence of the Osamu Utsumi uranium mine, comprise the study sites of the Pocos de Caldas Project.

Later major evolutive states of the Pocos de Caldas Complex involved the emplacement of mafic-ultramafic dyke rocks (lamprophyres) and the onset of lateritic and allitic weathering resulting (at the uranium mine) in the supergenic redistribution and formation of redox fronts related to uranium enrichments.

The regional rock studied were focussed towards the "status quo" properties of the intermediate nepheline suite with respect to the subsequent more local hydrothermal and final weathering related processes. They included petrographic, mineralogical, geochemical and isotopic studies, in addition to the measurement of the rock physical parameters. Results showed very little variations for the studied intrusive, subvolcanic and volcanic nepheline syenites. The lack of a major differentiation series may be seen as an argument for a short emplacement history of the intermediate nephelenic suite. Previous and present radiometric age measurements suggest a time span of about 15 m.y. for emplacement, much too long if compared to modern volcanoes. The end of the magmatic and hydrothermal-mineralizing events could be fixed by the Ar/Ar age of 76 m.y. of an unmineralized lamprophyre dyke intrusion at the site of the uranium mine.

Mineralogy, petrology and geochemistry of the Poços de Caldas analogue study sites, Minas Gerais, Brazil.
I: Osamu Utsumi uranium mine.

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Abstract

The Osami Utsumi Uranium mine is located on the border of a minor cilcular structure in the SE region of the Pocos de Caldas Complex. The open pit mine has a subcircular form with a mean diameter of some 800 m and exposes (from oldest to youngest) subvolcanic porphyritic phonolites as predominant rocks. that occur in multiple mutual intrusions. The phonolites were intruded by plutonic nepheline syenites that are the rocks second in abundance. Within the associations of phonolites and nepheline syenites were emplaced subvolcanic. strongly porphyritic pseudoleucite phonolites as minor intrusive bodies. Very rare rocks are aplitic, hololeucocratic phonolites in narrow dikes that may contain sporadically pseudoleucite phenocrystals. All these rocks are of leucocratic to hololeucocratic compositions with total contents of mafic minerals ≈35 and ≈5 vol. %, respectively. Phonolites and nepheline syenites were affected by intensive K- and S-rich hydrothermal activity. The hydrothermalism caused potassic alteration and pyritization, transforming the mine rocks into so-called potassic rocks (normally K_2O *〉 12 wt. %) with an anomalous background-grade U-Zr-REE mineralization of the dissiminated type. In the course of the hydrothermal alteration were formed, in recurrent processes, magmatic breccias obeing to the structural controls of an irregular shaped breccia pipe. Breccias are of the subvolcanic condiut type, predominating matrix poor types and form tabular bodies of*

high-angle to vertical positions. The fragment are of all the country rocks and vary widely in size, from metric to millimetric. Most breccia formed under hydrothermal P-T conditions but there exist breccias with truly magmatic matrices, too. The matrix phonolites are of volatile rich effusive lavas and show strong vesiculation and flow textures. Most are hololeucocratic, beer sparse pseudoleucite phenocrysts and may grade with decreasing fragment contents into variably xenolithic phonolites. The breccias were affected by the potassic alteration and pyritization, too, and are the main site of a higher grade U-Zr (REE) mineralization of the stockwork type.

The youngest magmatic event in the mine is represented by the emplacement of a suite of mafic-ultramafic lamprophyre dikes that cut through the hydrothermally altered phonolites, nepheline syenites and breccias. One dike could be dated radiometrically and defined a minimum age for the end of the evolution of the hydrothermally altered and U-mineralized nephelinic rocks and breccias of 76 m.y.

Later stages of the geological evolution of the sites of the mine included the inset of weathering and the development of redox fronts. The fronts are reaction zones of the pyritized and U-mineralized rocks with atmospheriles charged oxidic ground waters. They have roll front characteristics and caused supergenic redox front related U-mineralizations superimposed to the hydrothermal ones. The rocks above the redox front are characterized by reddish colours due to overall hydrous ferrix oxides (HFO) pigmentations and are called oxidized (potassic) rocks and breccias. The rocks below the redox fronts are termed reduced rocks and their colours are light-greyish due to the overall presence of disseminated silfides - mainly pyrite.

The main hydrothermal processes included the structural and chemical readjustement of the magmatic alkali feldspars into intermediate microcline of almost pure K-feldspar composition. Nepheline was replaced by mixtures of kaolinite and illite/sericite, and the magmatic aegirine-augitic clinopyroxene by assemblages of Nb-bearing TiO_2 *minerals, pyrite, smectite, chlorite and kaoloinite with or without relictic hematite. All the other mag-*

matic and postmagmatic minerals included and rare metal silicates, particularly giannettite, were replaced by variable assemblages of mainly illite/sericite, kaolinite, smectite, chlorite, TiO_2-minerals and pyrite. Hydrothermally precipitated minerals included additionally zircon and Zr-minerals, flourite, REE-minerals, U-oxides, minorcarbonate, sphalerite among others. All the hydrothermal minerals found in the disseminated, very low grade U-mineralized potassic rocks of the mine (hydrothermal assemblage) are found also in the breccia matrix and in the stockwork type higher grade U-mineralization of the breccia and fractured country rocks. However, the quantitative compositions are different and strongly variable (mineralization assemblages). In a general way in the mineralization assemblages all the ore minerals (including U-oxides), flourite, carbonate, Zr-minerals including zircon and the REE-phases are enriched and the common hydrothermal silicates, particularly K-feldspars are less frequent.

Most hydrothermal minerals were studied in detail with complementary methods including X-ray diffraction, cathode luminescence and electron beam techniques, among others.

A genetic model for the magmatic and hydrothermal evolution of the site of the mine includes subsequent emplacement of the main nepheline rock suite followed by down cooling and deuteric alterations probably under oxidic conditions; relictic hematite in pyrites of reduced potassic rocks are quite common. Minimum temperatures of the autohydrothermal stage of deuteric alterations were well within the kaolinite field, i.e. probably well below 200 °C. The inset of the hydrothermal alteration caused wide spread kaolinization and overall disseminated pyritization. Potassic alteration followed and included illite/sericite and K-feldspar formation, continued pyritization and Zr-, REE- and U-oxides formation among others in the course of increasing temperatures. Fluid inclusion studies of fluorites indicate minimum temeratures for this stage in the range of 210 °C - 260 °C. Maximum temeratures were attained during the culmination of potassic alteration and may have been in the range $>$260 °C to $>$360 °C as indicated by fluorite-fluid inclusions and illite crystallinity data respectively. Temperatures possibly *were already decreasing during the subsequent main formation of Zr-, U-oxides and REE-minerals and the associated fluorite generation (minimum T) 210 °C. The hydrothermal process acted in the country rocks of the mine by grain boundary infiltration, as show the homogeneous textural features of the mineral replacements and neo-formations.*

Most probably in the time period subsequent to the culmination of potassic alteration at the site of the mine volcanic explosive activity was reinitiated and led to the formation of the breccia pipe. Peak temperatures were magmatic however restricted to the less frequent high temperature breccias with volcanic (strongly vesiculated) phonolite matrices. Most breccias formed under hydrothermal conditions and probably in the presence of highly inhomogeneous fluids as indicated by the variable composition of texturaly penecontemporaneous mineralization assemblages that occur closely associated in the breccia matrices and the rock fractures. However, the general charcteristics of these fluids were further on potassic and sulfidic.

Comparative studies of the breccia and country rocks permitted the distinction of pre-breccia, syn-breccia and post-breccia stages of the hydrothermal and U-mineralizing evolution. All the three stages caused the deposition of distinct generations of pyrites that were separated and studied for S-isotopic compositions together with A. Fallick - SURRC. Results show that the three stages precipitated isotopically homogeneous pyrites with S lying in the range of $\delta^{34}S$ *of +1 to -3‰ CDT. This corresponds well with an origin of the hydrothermal and mineralizing fluids from a mantle derived magmatic source.*

The mineralogical studies of the lamprophyre dikes that cut thruogh the hydrotermalized and U-mineralized rocks strengthen the geological evidence: the lamprophyres were not affected by the potassic-sulfidic hydrothermal processes. The mafic minerals, otherwise extremely susceptible to pyritization, are completely fresh. The lamprophyres are mantle derived rocks of explosive and highly fluidized emplacement and carry very abundant cognate xenoliths of mainly pyroxenitic but also peridotitic and carbonatitic compositions. Country rock xenoliths are of reduced potassic rocks but in general *more seldom.*

The redox front mineralogy includes on the reduced side the precipitation of secondary supergenic U–oxides as nodules and coatings of rock fracture planes together with the formation of a secondary generation of pyrites and of Cds–greenockite exclusively inside the nodules. U–oxides are uraninite of low crystallinity. A zone of variable width (of 0–10 cm) separates the region with U–oxides from the front of HFO–mineral precipitation. This zone is still reduced as indicated by the presence of pyrite but U–oxides are already totally dissolved. On the oxidized side rocks are free of pyrite, fluorite, barite, other sulfide minerals as sphalerite, MoS_2–jordisite, carbonates and obviously U–oxides; in contrast they are slightly enrichedin clay minerals (5–10 vol %) particularly kaolinite. In some cases (i.e. redox front RF.1) the formation of sulfates, probably of iron sulfates of the jarosite type in a narrow (centimetric) zone directly adjacent to the RF may be suspected from geochemical evidences. Such sulfates have high capacity to incorporate structurally heavy metals including noble metals and radioactive ones.

A second generation of U–nodules, termed "massive nodules" occurred in the mine in specific zones within the environment of oxidized rocks. They show regular compositional zoning and similar mineralogical and geochemical characteristics as the redox front related nodules just strongly enhanced. U–oxides from massive zones reaching)10 –)30 vol % and show cryptocrystalline interstitial and colloidal very low temperature growth structures. Second generation pyrites are more abundant and more coarse grained and CdS–greenockite too. Various pyrite generations were separated and analyzed for the isotopical S–composition. Pyrites of the silicate cores of the nodules are similar to the hydrithermal pyrites of the reduced potassic rocks. Second generation pyrites of the massive pitchlbende zones are isotopically lightest with $\delta^{34}S$ of –12 –15‰ CDT indicating probably biogeochemical processes involved in the U–nodules formation. From the collected data a model of contractive growth is proposed for the massive nodulse. The process started with a part of a mineralized redox front that was totally ocluded in the environment of oxidized rock by more rapid *downward progression of the main redox front in adjacent rock portions. The isolated redox front portion was then progressively, concentrically, digested within the oxidezed rocks with progressive decrease of total volume (contraction) and consequent inward thickening (growth) of the zone of U-precipitation. A part of reduced country rock forms the silicate core of the nodules. This model seems in reasonable agreement with the data of Ken Osmond who dated (radioactive desequilibria method) two of such nodules and found at the outer and inner borders of their massive pitchblende zones always the youngest compositions that may be interpreted respectively as dissolution and reprecipitation.*

Geochemical main, trace and RE element studies were performed with different methods (XRF, ICP-OES, wet chenical, others) of: (I) the reduced potassic rocks of disseminated - anomalous backgroundgrade - U-mineralization (i.e. the normal reduced hydrothermalized country rocks of the mine), (II) hydrothermalized rocks and breccias containing higher grade stockwork type U-mineralization, (III) of various redox front profiles, (IV) of the oxidized rocks above the redox fronts, and (V) other more rare lithologies including two lamprophyre dikes and the only incipiently hydrothermalized phonolite country rocks of the NW-walls of the mine. Datas will be presented using two sets of graphics: chondrite and primordial mantle (for K, Rb, P) normalized spider diagrams of incompatible elemnts and chrondrite normalized REE-plots to illustrate general enrichment factors, equivalent diagrams normalized using the mean values of the region country rocks to illustrate process specific variations. Some of the results included the general enrichment of incompatible elements in the reduced country rocks of the mine; the general immobility of the REE in the redox processes except perhaps for a slight reduction of HREE; the characteristic enrichment of the HREE with the hydrothermal U-mineralization and the enrichment of intermediary and HREE in the redox front related U-mineralization.

Mineralogy, petrology and geochemistry of the Poços de Caldas analogue study sites, Minas Gerais, Brazil.
II: Morro do Ferro.

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Abstract

The Th-REE-deposit at Morro do Ferro, located centrally within the Pocos de Caldas Alkaline Complex, is of supergene origin formed under silicatic and allitic weathering conditions. The orebody, located at the surface of strongly weathered, lateritic material, forms NW-SE elongated argillic lenses that extend from the top to the hill downwards along the south-eastern slope. Numerous, partly oxidized magnetite veins of variable thickness form a magnetite stockwork which has helped to resist erosion and preserved Morra do Ferro as the highest point within the Pocos de Caldas caldera.

Mineralogical and geochemical data are presented from two drillcores, MF 10 and MF 12. MF 10 penetrates the orebody and the underlying weathered material; bastnaesite, monazite, cheralite, goyazite, thorianite and thorite are the most important REE- and Th-bearing phases of the orebody. A wide variety of secondary Th- and REE-phosphates, silicates and oxyhydroxides occur in minor amounts, becoming increasingly more abundant in the underlying weatheredmaterial, composted mainly of kaolinite and illite.

MF 12, which is located at the south-eastern base of the hill, penetrates the lateritic weathering cover before encountering hydrothermally altered phonolite at a depth of 27.5 m. The weathering cover consists mainly of-kaolinite, gibbsite, hydrous ferric oxides and illite. Prior to weathering the phonolite underwent a potassium metasomatism leading to the formation of low-temperature K-feldspar. Mineralogical features, together with the REE-fluorite-U-Th-vein type mineralization, are typical for fenitizised

rocks. This type of mineralization, and the alteration features of the phonolitic wallrock, strongly suggest a carbonitite intrusion as being the primary source of the Th and REE's at Morro do Ferro.

Major and trace element concentrations differ markedly between the orebody and the underlying weathered material, compared to the lateritic cover above the phonolite. In the orebody, but more pronounced in the weathered material, Ce is highly correlated with Th and U whereas La correlates with Nd and Y. In the lateritic cover and the phonolite of MF 12, the LREE's show a high degree of correlation but not with TH and U. Mass balance considerations reveal a residual enrichment of Th and LREE in the orebody and the underlying weathered material, in addition to the laterite which overlies the phonolite. Mineralogical and geochemical differences in the weathered material from both drillcores clearly demonstrate two different parent rocks.

Isotopic geochemical characterization of selected nepheline syenites and phonolites from the Poços de Caldas alkaline complex, Minas Gerais, Brazil

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Abstract

This paper presents and discusses the isotopic data of the Hydrothermal Studies of the Poços de Caldas Natural Analogue Project. The purpose of this study was to elucidate the mass transport of appropriate elements and isotopes associated with hydrothermal mineralization and alteration at the Osamu Utsumi uranium mine, particularly as applicable to radwaste isolation concerns in the U.S. nuclear waste program.

Research efforts were focused to study the thermal, chemical, and hydrologic nature of the paleohydrothermal regime associated with a breccia pipe at the Osamu Utsumi mine. Geochemical, geochronological, and petrological characterization studies of related but unaltered regional nepheline syenite and phonolite were also performed.

The studied regional rocks have a vertically elongated δD, $\delta^{18}O$ *pattern which possibly indicates meteoric water/rock interaction. Regression of Rb-Sr whole-rock data for the regional nepheline syenite and phonolite samples did not produce isochrons. An internal, mineral separate isochron regression from nepheline syenite sample Ns-7, considered representative of unaltered nepheline syenite of the Poços de Caldas plateau, yields an age of 78(3) Ma, and an initial* $^{87}Sr/^{86}Sr$ *ratio of 0.70511(1). The moderate initial* $^{87}Sr/^{86}Sr$ *ratios of the regional nepheline syenites are possibly indicative of a mantle source for the alkaline magmatism, with some incorporation of old, high Rb/Sr crustal material. The greater than mantle values of* $\delta^{18}O$*, if not due to surficial processes, also appear to require some assimilation of crustal material. Sm-Nd data for the regional rocks do not define any isochrons, although the nepheline syenite samples conform very well to a calculated model isochron for 78 Ma and an initial* $^{143}Nd/^{144}Nd$ *of 0.512359. The regional phonolite samples lie markedly off this isochron. This open system behavior is probably due to the phonolite samples having different initial* $^{143}Nd/^{144}Nd$ *values. Even so, all regional samples lie within the "Mantle Array" trend. Their location within* $\epsilon_{Nd} - \epsilon^{Sr}$ *space indicates an asthenospheric MORB-type source magma also contaminated by*

continental igneous and metamorphic rocks (e.g., the Precambrian schist surrounding the Poços de Caldas plateau).

The rocks studied at the Osamu Utsumi mine from the F4 drillcore, have experienced variable degrees of hydrothermal mineralization and metasomatism, and deep weathering. The hydrothermally altered rocks have a quite pronounced δD *shift, with only a slight* $\delta^{18}O$ *shift.*

The 5D-$\delta^{18}O$ *trend of the hydrothermally altered F4 samples likely reflects the variability of temperature, hydrologic flow, and therefore water/rock interaction and isotopic exchange in the paleohydrothermal regime.*

Regression Rb-Sr whole-rock data for subsamples of the F4 413 nepheline syenite xenolith sample yield an age of 76(1) Ma, and an initial $^{87}Sr/^{86}Sr$ *ratio of 0.70530(11). Due to the marked hydrothermal alteration and metasomatism of this sample, the Rb-Sr isotopic system is interpreted as reequilibrated and thus the regressed age is the age of the hydrothermal event. Using a* $(^{87}Sr/^{86}Sr)$*, versus 1/Sr mixing diagram, distinct trends are seen for hydrothermal alteration, mineralization, and weathering.*

Again, the nepheline syenite subsamples of F4 413 do not define an Sm-Nd isochron, but conform very well to a calculated model isochron for 78 Ma and an initial $^{143}Nd/^{144}Nd$ *of 0.512365. The Sm-Nd isotopic data also exhibit likely disturbance by the hydrothermal, metasomatic alteration.*

A lamproite dike which crosscuts the hydrothermal alteration in the Osamu Utsumi mine gives an age of 76(1) Ma, which is essentially the same as the F4 413 Rb-Sr age.

Geomorphological and hydrogeological features of the Poços de Caldas caldera and the Osamu Utsumi mine and Morro do Ferro analogue study sites

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Abstract

The Osamu Utsumi mine and Morro do Ferro study sites lie within the Poços plateau which is roughly circular in outline with a diameter of 30 km and some 800 km^2 in area. Its general altitude lies between 1300 and 1600 m. The plateau is the eroded form of a caldera which was initially intruded some 80 million years ago.

Geomorphologically, both sites occupy water shed areas adjacent to small streams in the centre of the Poços plateau. The climate of the area has a marked wet season from November to April and dry the rest of the year. The streams are ephemeral in their upper reaches tending to dry up in the dry season as they are fed by a declining base flow. In the wet season they exhibit flash floods fed by high intensity rainfall causing overland flow. The wet season also provides recharge to the groundwater. Natural slopes are steep and the original vegetation was thin forest cover. This is now restricted to the valley bottoms and the usable slopes have poor quality grass cover used to graze cattle. The plateau is a stable feature and its surface has been eroding at an average rate of 12 m per million years over 50 million years.

The mine geology is dominantly volcanic to subvolcanic/phonolites that have been hydrothermally altered. Fracturing of the rock is extensive. Downward diffusion of oxygen in groundwaters during deep weathering has produced a distinct redox zone seen as a colour change from green/grey to brown/yellow. Morro do Ferro has a more weathered version (laterite/clay) of the same geology penetrated by magnetite breccia dykes. Whilst the area surrounding Morro do Ferro remains untouched, that around the mine has been seriously disturbed by mining activity which has penetrated the water table. The existing mine has modified groundwater flow patterns and disturbed the movement of oxidising and reducing waters.

Chemical and isotopic composition of groundwaters and their seasonal variability at the Osamu Utsumi and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.

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Abstract

Groundwaters and a few surface waters were collected over a period of 3 years from two natural analogue sites near Poços de Caldas, Brazil: the Osamu Utsumi uranium mine and the Morro do Ferro thorium/rare-earth deposit. These were analyzed for major constituents, several trace elements, tritium, deuterium and ^{18}O*, to provide hydrochemical data for the modelling objectives as defined within the natural analogue study programme. The groundwaters are a* K-Fe-SO_4 *type which classifies them as a highly unusual composition related to the weathering of a hydrothermally altered, mineralized complex of volcanic to sub-volcanic phonolites.*

A subset of selected constituents (Fe[II], Fe[total], SO_4*, pH, Eh, alkalinity, F and U) were monitored to gain detailed information on the seasonal variability. Seasonal patterns were only apparent from the very shallow groundwater data, but a trend of continuously increasing dissolved solids for the furthest downgradient sampling point in deep groundwater, indicates a growing plume of water affected by pyrite oxidation but without the residual acidity. Tritium and stable isotope measurements indicate that all groundwaters are of meteoric origin and are not affected significantly by evaporation or by water-rock interactions. Recharging groundwaters at both study sites demonstrate infiltration of water of less than 40 years in age, whereas deep groundwaters are below 1 TU but still contain detectable tritium. These deeper groundwaters may be interpreted as being of 40-60 years in age, resulting from an admixture of younger with older groundwaters.*

Natural radionuclide and stable element studies of rock samples from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.

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Abstract

This report describes a study of the distribution and behaviour of natural radionuclides and selected stable elements at the Poços de Caldas and Morro do Ferro natural analogue study sites. At Poços de Caldas, the study was focussed upon investigation of the behaviour of natural decay series radionuclides and stable elements at the redox fronts which exist in the mine. Uranium nodules from the mine were also analysed for natural decay series radionuclides in order to characterize their ages and growth rates and for natural plutonium. At Morro do Ferro, the objective was to provide additional information on the geochemical behaviour of thorium, uranium and the light rare earth elements and to relate this to the groundwater flow pattern in an attempt to evaluate the degree of mobilization of these species.

A summary review of these aspects of the geochemistry of natural decay series radionuclides relevant to the interpretation of radioactive disequilibrium is provided along with a detailed treatment of mathematical modelling of natural

decay series disequilibria in rock-water interactions. The overall study comprised a number of discrete subprojects carried out in five different laboratories and each of these is described in detail. In addition to constituting a self contained study, the results and conclusions of this work were also used as an input for modelling studies and other aspects of this integrated research programme.

The natural decay series studies at the Osamu Utsumi mine confirmed the generally greater solubility of U^{6+} and Ra than U^{4+}, Th and Pa in groundwater. The results further indicated that at the position of the drillcore studied, the long term direction of groundwater flow had been downwards, along the line of the main fissure system, rather than upwards as is presently observed.

Dissolution of uranium and other elements at the redox fronts followed by diffusive movement into both the oxidized and the reduced rock is identified as the mechanism giving rise to the observed concentration profiles about the redox fronts. Deposition of uranium, either as thin, dispersed coatings on other minerals, or as discrete nodules, occurs in the reduced rock as a consequence of the reduction of U^{6+} to U^{4+}. Deposition of uranium, almost certainly by uptake on iron oxides, is also identified as a significant retardation process in the oxidized rock. Some of the uranium nodules are young (on a 10^5-10^6 y timescale) and exhibit growth rates of 1.8-2.6 cm in 10^6 y, whereas others are old on this timescale and exhibit equilibrium within the natural decay series. The time required for growth of nodules in the reduced rock is estimated to be of the order of 10^5y at least and a similar time is required for dissolution of micronodules stranded in the oxidized rock following passage of the redox front.

The natural ^{239}Pu content of a nodule from the reduced rock was measured as U$2.3 \pm 0.7 x 10^8$ atoms per gram, consistent with a state of secular equilibrium between ^{238} and ^{239}Pu. The study thus reveals that uranium (plus daughters) and plutonium are chemically stable in the form of nodules in the reduced rock for a time of at least 10^5 years.

One of the redox fronts studied was concluded to have been effectively static (on a cm scale) for a time of at least $7x10^5$ y, while the natural decay series data for the other fronts were consistent with rates of movement in the range 2-20 m in 10^6 y, in good general agreement with the estimated rate of regional erosion.

Dissolution and redeposition of thorium was observed, with preferential deposition on the reduced sides of the redox fronts. The degree of redistribution of thorium in this way is estimated to be at least two orders of magnitude less intense than the corresponding redistribution of uranium. Separation of uranium from thorium is observed as the redox fronts moves downwards and the degree of separation increases with increased length of flow path of the groundwater.

Summary data are provided for a range of stable elements, including the rare earths, which support the observations mode above for uranium and indicate that the zone around the redox fronts contains generally elevated concentrations of most elements in conjunction with active dissolution at the front. This results in a variety of distributions of different elements about the redox fronts. The redox fronts thus represent an initial zone of retardation which would be a positive factor in far-field radionuclide migration considerations. However, a negative aspect of this situation is that the zone of enhanced concentrations moves in response to movement of the redox front and, given a sufficient distance of travel, could result in a breakthrough of high concentrations of radionuclides into the near surface environment.

NATURAL SERIES NUCLIDE AND RARE-EARTH ELEMENT GEOCHEMISTRY OF WATERS FROM THE OSAMU UTSUMI MINE AND MORRO DO FERRO ANALOGUE STUDY SITES, POCOS DE CALDAS, BRAZIL

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ABSTRACT

Data are presented on natural series radionuclides, rare-earth elements and noble gases in pre-filtered (<450 nm) subsurface and groundwaters from the 'Osamu Utsumi' uranium mine and the 'Morro do Ferro' thorium-REE-deposit, both situated in the 'Pocos de Caldas' plateau in the state of Minas Gerais, Brazil.

In the uranium mine, very high concentrations of U (until 10 mg/l) were measured in subsurface waters. In groundwaters (60 - 120 m), concentrations of this element are typically between 3 and 10 ug/l. The reduced concentrations of uranium in the aquifer rock of the 'Morro do Ferro' are reflected in the considerably lower concentrations of this element in waters from this environment. The concentrations of Th-232 in groundwaters from both sites are very low and generally <0.1 ug/l, however, can be higher by a factor of 100 or more in superficial waters rich in humic compounds (Morro do Ferro) or sulfate (Osamu Utsumi mine).

Pronounced radioactive disequilibria between U-234 and U-238 were measured in groundwaters and which are characterized by an excess of U-234 due to preferential leaching of this isotope and/or recoil effects. An increase of the U-234:U-238 activity ratios with sampling depth (1.0 - 1.2 for superficial waters and up to 2.7 for groundwaters) has been measured and which is apparently caused by a slight decrease in the environmental redox potential. Due to the extreme low solubility of thorium and its strong tendency for sorption on suspended particles (mainly composed of hydrous ferric oxides), the Th-230:U-234 ratios in groundwaters are also very low (<0.01).

Rare-earth element concentrations in groundwaters from both sites are typically in the range between 1 - 50 ug/l for the LREE (La, Ce, Nd) and 0.001 - 0.1 for the HREE (Ho-Lu), but can be much higher in superficial waters of high complexation capacities, similar as observed for thorium. The chondrite normalized distribution patterns of the REE in water samples (and in suspended particles) are similar as those noticed in the bedrock surroundings, indicating non-preferencial dissolution (and sorption) of these elements. An exception, however, is Ce which shows a

very characteristic depletion in oxidising subsurface waters of both sites, probably related to the much lower solubility of Ce-IV species in natural waters.

Concerning the mobilisation of thorium and the rare-earth elements via 'solution' phase, the data obtained in this study provide further support that solubility limitations (Th) and strong affinities for sorption (Th and the REE's) on particulate and colloidal matter are efficient mechanisms, which may restrict the dispersion of these elements (and possibly also that of their transuranium analogues) in porous media to small-scale dimensions. This is best seen by the absence of any significant contribution of the 'Morro do Ferro' deposit with its 30,000 t of Th and its nearly 100,000 t of LREE's, to the concentrations of these elements in drainage waters (<450 nm) collected in about 100 m of distance from the mineralisation zone.

Chemical and physical characterisation of suspended particles and colloids in waters from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.

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Abstract

Data are presented on suspended particles and colloids in groundwaters from the Osamu Utsumi mine and the Morro do Ferro analogue study sites. Cross-flow ultrafiltration with membranes of different pore sizes (450 nm to 1.5 nm) was used to prepare colloid concentrates and ultrafiltrates for analyses for major and trace elements and U- and Th-isotopic compositions. Additional characterization of colloidal and particulate material was performed by ESCA, SEM and X-ray diffraction. The results obtained indicate the presence of low concentrations (<1 mg/l) of colloids (1–450 nm) in these waters, composed mainly of iron/organic species. Minor amounts of U and some other trace elements, and significant amounts of Th and REEs were associated with these colloids. U-isotopic measurements indicate element exchange equilibrium between aqueous, colloidal and suspended particle phases. Suspended particles (>450 nm) in the waters show the same trends as the colloids in respect of U, Th and REE associations, but elemental concentrations were typically higher by a factor of 1,000 or more. Calculated association ratios are in the order of 10^4 *to* 10^5 *for U,* 10^5 *to* 10^6 *for the REE and* 10^6 *to* 10^7 *for Th. In waters with low ph and high sulphate content, these ratios are considerable lower. Due to the low concentrations of suspended particles in groundwaters from the Osamu Utsumi U-mine (<0.5 mg/l), these particles carry only a minor amount of U and REEs (<10% of the total concentration of the unfiltered groundwater), but a significant, usually predominant, fraction of Th (30–70%). The suspended particle load in groundwaters from the Morro do Ferro environment is typically higher than in those from the mine by a factor of 5 to 10. This suggests that U and the REEs could be transported predominantly by particulate matter. However, there is chemical and mineralogical evidence that these particles, composed mainly of Fe(III) oxyhydroxides and humic compounds, are formed 'in situ' in the groundwaters and have a low capacity for migration.*

Microbiological analysis at the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil.

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Abstract

The Poços de Caldas project is a wide ranging natural analogue study focussed on a number of areas of concern in the performance assessment of the disposal of radioactive waste. Part of the work has involved characterising microbial populations and their influence in various processes. Core material and groundwaters have been sampled for microbiological content at various depths from boreholes at the Osamu Utsumi open pit uranium mine and Morro do Ferro Th/REE ore body. Microbes were found in all samples but numbers do not appear to be related to depth. Analyses of groundwaters gave higher numbers than with solid material and demonstrated the presence of sulphur cycle bacteria.

These observations have been compared with predictions of a model used in performance assessment to calculate the maximum biomass/microbial activity based on constraints set by available nutrients and energy. The main conclusions of this analysis are:

i) *Low microbial activities can be supported by the energy and nutrients supplied by alteration processes at or around the redox front. The maximum annual production of ≈0.01 – 0.1 g biomass (dry)/m^2 of redox front is in reasonable agreement with observed standing populations.*

ii) *The presence of high concentrations of sulphate reducing bacteria around the redox front indicate a complex sulphur geochemistry which may be predominantly microbially catalysed and could explain the nodular form of pitchblende concretions and the presence of secondary pyrite.*

iii) *There is little trace element mobilisation by organic byproducts and the main rôle of microbes in this system is to catalyse specific redox reactions.*

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Testing of geochemical models in the Poços de Caldas analogue study

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Abstract

In order to test the geochemical models used in repository performance assessment, modelling groups were provided with selected major element analyses of Poços de Caldas groundwaters and asked to predict 'blind' the solubility, speciation and limiting solid for a number of trace elements. This report documents these predictions and compares them to field analyses. These tests illustrate particular strengths and weaknesses in current models / databases and allow recommendations for amendments / improvements to be made.

Testing models of redox front migration and geochemistry at the Osamu Utsumi mine and Morro do Ferro analogue sites, Poços de Caldas, Brazil

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Abstract

Redox fronts occur at a number of locations in repository systems and models have been established to describe their chemical evolution and spacial development. Such models can be tested against detailed observations of the well developed redox fronts at the Osamu Utsumi mine.

Simple scoping calculations can explain the formation of redox fronts in very general terms but greatly simplify the processes known to be occurring at such fronts. Coupled transport / chemistry models can provide a better simulation of the fronts, but these are really interpretative models which do not display any convincing predictive abilities. They tend to be rather poor, in particular, in simulating trace element chemistry in either solution or solid phases.

Interpretative modelling of microbial activity, natural series profiles and trace element distributions, give strong indications of the reasons for the limitations of the chemical modelling. The rôle of microbial catalysis seems to be very significant in such systems, particularly affecting the redox chemistry of sulphur. Natural series measurements

indicate very slow redox front movement at particular sites which could be due to precipitation processes limiting accessible porosity, a point not especially considered in any of the models. Finally, the trace element distributions strongly suggest immobilisation of many elements as co-precipitates or solid solutions in secondary iron minerals, again a process not considered by current models.

From the point of view of repository performance assessment the main conclusions of this study are: a) the current generation of coupled transport / chemistry models poorly simulate a moving redox front, b) in general, the models tend to over-predict rates of front movement and thus, in most cases, could be considered as "conservative", c) the models cannot simulate trace element removal by co-precipitation, which would again be generally conservative, and d) microbiology appears to play an important rôle in defining the redox chemistry of the front, particularly for sulphur.

Near-field high temperature transport: Evidence from the genesis of the Osamu Utsumi uranium mine, Poços de Caldas alkaline complex, Brazil.

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Abstract

The chemical, isotopic, and mineralogical alteration which occurred during primary uranium ore deposition at the breccia pipe-hosted Osamu Utsumi mine, Poços de Caldas, Brazil, was studied as a natural analogue for near-field radionuclide migration. Chemical and isotopic alteration models were combined with finite difference models of the convective cooling of caldera intrusives. The modelling indicates that the intense chemical, isotopic, and mineral alteration of the Osamu Utsumi breccia pipe requires the circulation of $>10^5$ *kg/cm*^{2} *of boiling hydrothermal fluid* $>220°C$ *through the pipe. The circulation can be driven by heat from a 6 km diameter intrusion extending to 10 km depth. Even with this large amount of circulation concentrated in the permeable breccia pipe, uranium solubilities must be 2 1/2 orders of magnitude greater than indicated in the most recent experiments (and more in line with previous estimates) to produce the primary uranium mineralization at the Osamu Utsumi mine.*

The same models applied to a high temperature waste repository show that heat from radioactive decay will produce a hydrothermal circulation system remarkably similar to that studied as a natural analogue at Poços de Caldas. The depth of fluid convection induced by the repository will be 5 to 10 km, the maximum temperature $\sim 300°C$*, the lifetime of the high temperature phase a few 1000's of years, and boiling will occur in the repository and cause most of the alteration of the waste repository. The physical analysis emphasizes the importance of permeability on a 10 x 10 x 10 km scale in controlling the potential amount of circulation through the repository.*

Application of the chemical models successfully used to interpret mineralization and alteration at the Osamu Utsumi mine to the waste repository shows that even in the worst case (waste implaced in a permeable host rock and no measures taken to inhibit flow

through the repository) the amount of hydrothermal alteration in the repository will be ~0.1% of that in the breccia pipe at Osamu Utsumi. Assuming no barriers to uranium mobility, uranium precipitation above the repository will be 0.05 ppm (rather than 50 ppm), hydrothermal alteration 0.03 wt% (rather than 30 wt%), etc.

The analysis indicates that mineralogic alteration is extremely sensitive to thermodynamic data. Extrapolated prediction of mineralogic alteration (which may be necessary to predict the migration of radionuclides other than uranium, for example) probably cannot be based directly on even very carefully collected laboratory thermodynamic data. Natural complexities and data uncertainties will require calibration of the thermodynamic framework against mineralogic alteration observed in the laboratory or field by procedures briefly described.

Geochemical modelling of water-rock interactions at the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil

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Abstract

Geochemical processes involving water-rock-gas interactions have been modelled using groundwater compositions, mineralogical data, ion plots and computations of speciation, non-thermodynamic mass balance and thermodynamic mass transfer for two natural analogue sites near Poços de Caldas, Brazil: the Osamu Utsumi mine and Morro do Ferro. The main rock type is an alkaline igneous complex composed of volcanic and sub-volcanic phonolites that have been hydrothermally altered and highly weathered. This altered rock mass grades from a laterite at the surface to a saprolite and finally to unweathered, hydrothermally altered bedrock at depth. The mine site contains high concentrations of uranium and Morro do Ferro contains high concentrations of thorium and rare earths. The reaction models can reproduce the water chemistry and mineral occurrences and they were validated by predicting the masses of minerals precipitated and the pH of the final water. The model computations can also reproduce the pH and iron concentrations of the water samples during CO_2 *degassing and iron(II) oxidation from exposure to air. The results from the geochemical reaction models reveal that the dominant processes are production of* CO_2 *in the soil zone through aerobic decay of organic matter, dissolution of fluorite, calcite, K-feldspar, albite, manganese oxides, oxidation of pyrite and sphalerite, and precipitation of ferric oxides, silica and kaolinite. Recharge waters are undersaturated with respect to barite and discharging waters and deeper groundwaters are saturated to supersaturated with respect to barite demonstrating a strong equilibrium solubility control. Strontium isotope data demonstrate that sources other than calcium-bearing minerals are required to account for the dissolved strontium in the groundwaters. These may include K-feldspar, smectite-chlorite mixed-layer clays and goyazite.*

APPENDIX 2

Some posters presented at the meeting

Natural Analogue Studies and Performance Assessments in Finland

by

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SUMMARY

Three Finnish natural analogue studies are presented shortly, they deal with different aspects of disposal system in fractured rock. Native copper study touches on the long term stability of copper canister in granitic bedrock. Anion profile study deals with penetration depth of matrix diffusion in rapakivi granite. Palmottu uranium deposit is being studied as migration analogue in fractured granitic bedrock. An attempt is made to relate natural analogue studies to the disposal system and to evaluate the applicability of the results in performance assessments.

1. INTRODUCTION

According to current Finnish plans, spent nuclear fuel will be disposed of in fractured granitic bedrock at the depth of about 500 m. Spent fuel bundles will be encapsulated in copper canisters. Copper canisters will be placed in vertical deposition holes surrounded by compacted bentonite. Finally, all tunnels will be backfilled using a mixture of sand and bentonite. The safety of this concept is based on multiple barrier principle, Figure 1.

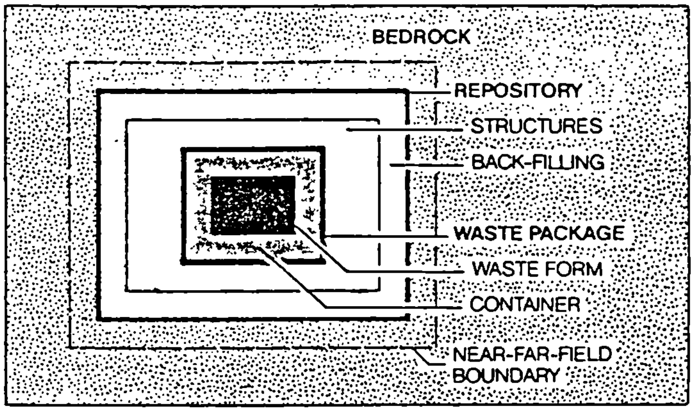

Figure 1. Principle of multiple barrier disposal system (Peltonen, 1987).

Safety assesments of the final disposal include many sources of uncertainty, some of which can be studied using natural analogues. There are several important safety factors of which natural analogues can give valuable information, e.g. solubility, radiolysis and the retardation of radionuclides in the geosphere. These factors depend on hydrochemical, hydrological, geochemical and other site-specific factors, so detailed background information is needed for the interpretation.

2. NATIVE COPPER

The applicability of <u>native copper occurrences</u> as stability analogues of copper canisters was studied at the Helsinki University of Technology. Most of the literature on native copper occurrences was reviewed. Microscopical and microanalytical studies on rock samples containing native copper were performed revealing that the metal shows no significant alteration (-Marcos, 1989). Although the Finnish bedrock mineralogy partly differs from that of the studied host-rocks of native copper, the crucial geologic conditions are similar. It can hence be concluded that the geological environments in Finland provide, in many places, geohydrological conditions favourable for the long lasting stability of metallic copper.

3. ANION PROFILES AROUND ROCK FRACTURES

Anion profiles in granite bedrock are being studied at the Technical Research Centre of Finland. Due to postglacial land uplift the island of Hästholmen on the southern coast of Finland started to rise from the Baltic Sea some 5000 years ago; the land uplift is some 3 mm per year at present. Rainwater infiltrated into the ground has formed a layer of fresh groundwater floating on top of the saline layer. The bedrock of Hästholmen consisting of coarse-grained granite has been studied by core-drilling and subsequent investigations for suitability of an underground repository for low and medium level reactor wastes.

Non-fractured core sections between pairs of water-conducting fractures were selected from drill cores. At present the water in those fractures is of low salinity. The long cores were sampled at intervals of about one meter. Each sample was crushed and the finer fraction was sieved out with 1 mm sieve. Also 1 cm thick core sections were taken. The fractions were then immersed in deionized water for three months after which period chloride and sulfate were analyzed from the water phase.

The salinity of the ground water is reflected to the anion concentration of the pore water. There can still be found regions, where the salinity in the pore water in the rock is still gradually decreasing in the scale of meters.

Fitting of a diffusion model to the experimental results was performed taking into account the development of the fresh water front in the past. Apparent diffusion coefficient giving a reasonable fit to the profiles is 2×10^{-9} m^2/s (see: Figure 2). This is an order of magnitude higher than measured in the laboratory, and also physically too high corresponding to the molecular diffusion coefficient in free water.

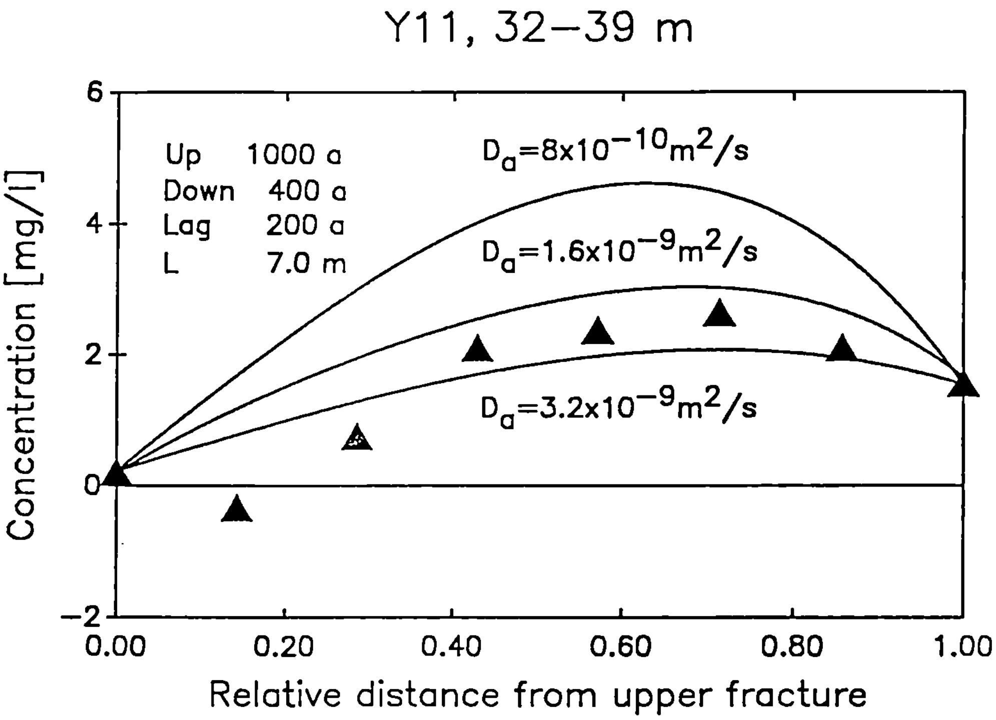

Figure 2. Measured chloride concentrations (triangles) and calculated diffusion profiles as a function of dimensionless depth for the examined section of the drill core Y 11. "Up" indicates the time, years from the present, when the salinity has in the upper fracture started to decrease to the background value. "Down" indicates the time when the salinity has in the lower fracture started to decrease to the background value. "Lag" is the time estimated for the water in a fracture to transform from saline to fresh. D_a corresponds to the apparent diffusion coefficient.

4. THE ANALOGUE STUDY OF PALMOTTU

Introduction

The applicability of the results of major international natural analogue projects to assess the safety of disposal of spent nuclear fuel in Finland is partly limited, as the deposits are not located in a crystalline, metamorphic bedrock which will be the case for a repository in the Finnish bedrock. The uranium deposit at Palmottu in Nummi-Pusula, southwestern Finland, is being investigated to study the function of common Finnish bedrock as a natural barrier for radionuclide migration. This aim includes the following main targets:

- to characterize the basic hydrogeological, petrological and mineralogical features
- to identify mechanisms and phenomena controlling the mobilization and transport of radionuclides
- to determine the time scales of radionuclide migration
- to quantify relevant mass-flows
- to interpret the results in relation to performance assessment.

The study is a part of the governmental research programme on the management of radioactive wastes financed by the Ministry of Trade and Industry. The co-operating research organizations are Geological Survey of Finland, University of Helsinki and Helsinki University of Technology.

General geology

The bedrock of the Nummi-Pusula area consists of Svecofennian schists and migmatite-forming microcline granites. The schists are metamorphosed and recrystallized sediments the original composition of which varied from arkose to graywake. The rocks in the study area itself consist of mica gneisses, quartz-feldspar gneisses, and pyroxene-bearing gneisses with abundant granitic veins and granitic interlayers or lensoidal bodies (see: Räisänen, 1986).

The Palmottu ore deposit

The Palmottu uranium deposit was discovered by airborne geophysical surveys conducted by the Geological Survey of Finland in the late 1970s (Räisänen, 1986). Altogether 62 holes with a combined length of 8100 meters were drilled during the beginning of 1980s. The holes were drilled approximately perpendicular to the strike of the rocks, and hence the drill cores contain all the rock types common to the area.

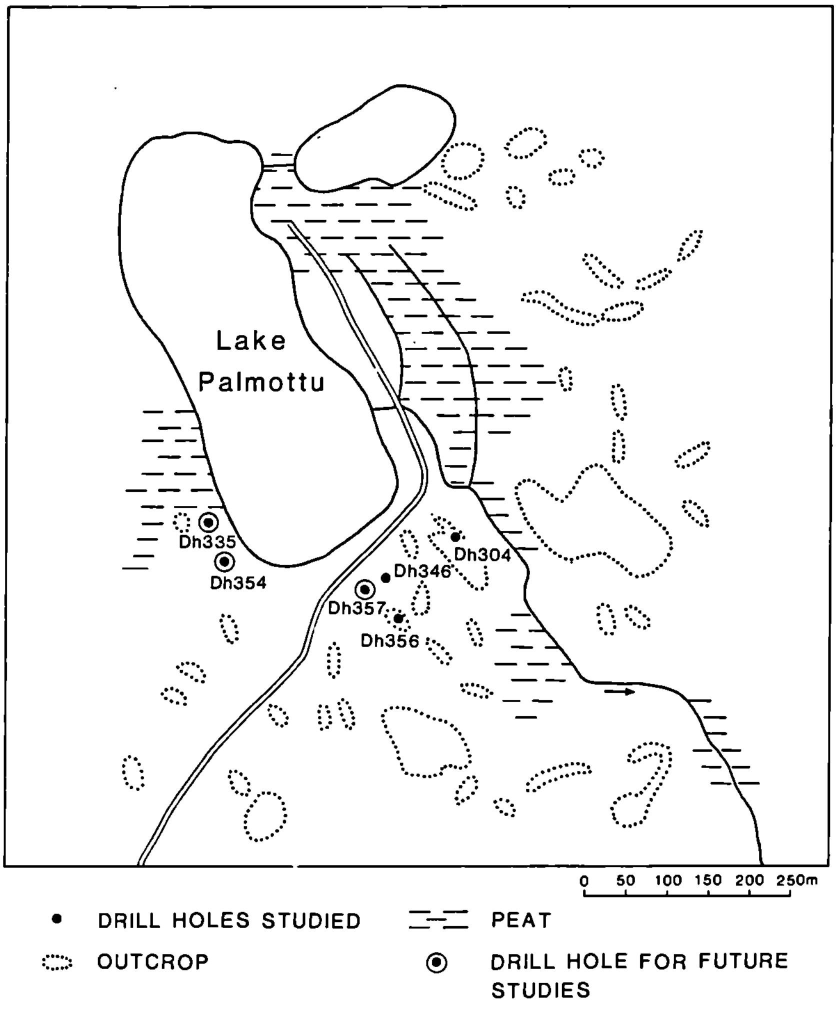

Figure 3. The location of the Palmottu study area, SW Finland.

Two types of uraniferous veins can be found in the Palmottu deposit: (1) a coarse-grained feldspar-quartz-biotite pegmatite and (2) a sheared granitic vein rich in quartz and biotite.

The predominant minerals in pegmatites are potassium feldspar, quartz, and biotite. Opaques, apatite, zircon, monazite, carbonate, tourmaline, and secondary clay minerals are the typical accessories. Quartz and biotite grains are fractured and variably recrystallized. Microfractures are common and some of them have fillings consisting of a mixture of iron sulphides, carbonates, micas, and uraniferous material.

The mica gneisses are composed of potassium feldspar, quartz, biotite and, plagioclase (An$_3$0-38). Apatite, zircon, monazite, carbonate, garnet, and clay minerals are common accessories. The gneisses show distinct orientation, and fracture cleavage is often well developed.

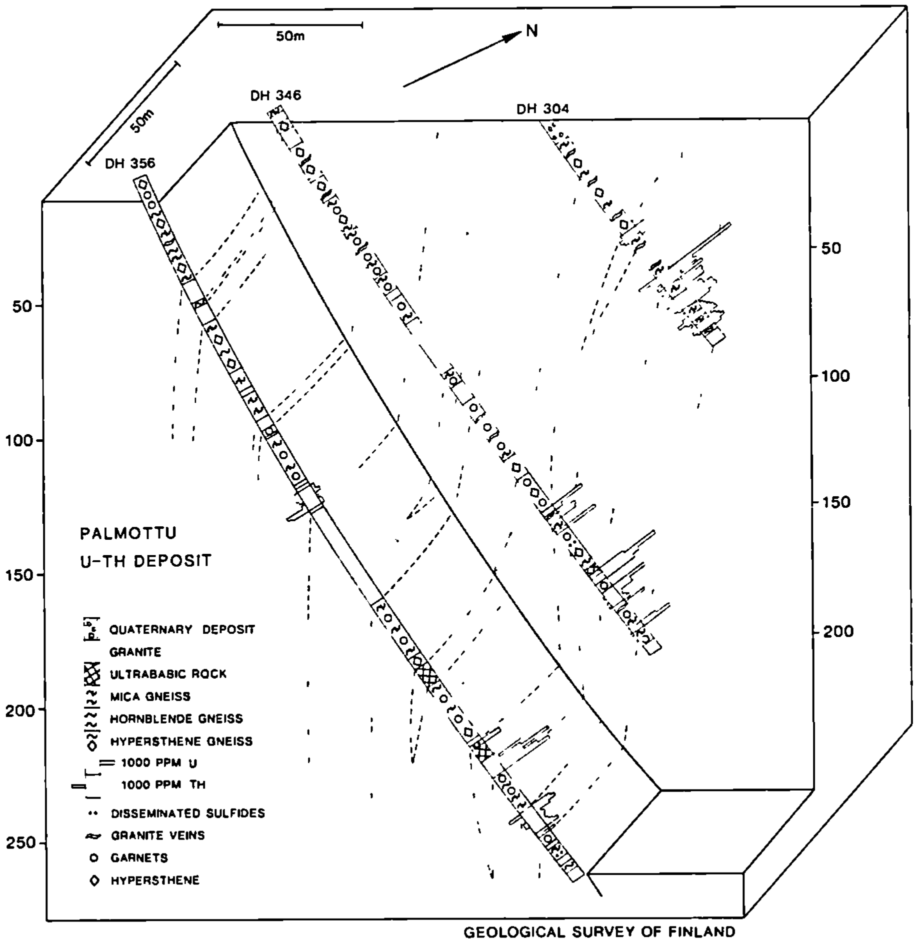

Figure 4. Lithologies encountered in drill holes 304, 346 and 356 with respective uranium and thorium contents (based on the unpublished results of E. Räisänen, the Geological Survey of Finland)

Uranium occurs mainly as uraninite which occurs as fractured subhedral grains often associated with biotite with an average grain size of less than 0.3 mm. The uraninite of the nearby Hyrkkölä mineralization has been dated at 1774 Ma, which makes it slightly younger than the late-orogenic intrusive rocks (1830 Ma) in the area (Räisänen, 1986).

Results

The methods used in the analogue study include mineralogical and petrographical studies, hydrological tests, groundwater chemistry, and various sophisticated radiochemical methods (Blomqvist et al., 1987; Jaakkola et al., 1989; Ruskeeniemi et al., 1989; Niini et al., 1990; Ahonen et al., 1990). Recently also geophysical and structural methods for fracture identification and classification have been introduced.

The studies have already given useful information about the behaviour of uranium in crystalline bedrock conditions. Redox conditions, as expected, seem to determine the occurrence of uranium in groundwater (Suutarinen et al., 1990). U concentrations decrease distinctly with depth (from 54 to 1.4 ppb), whereas the $^{234}U/^{238}U$ activity ratios strongly increase (from 1.3 to 3.7).

The studies on fracture coatings have given versatile information about the long term behaviour of uranium. The distribution of uranium in fracture lining minerals e.g. kaolinite, calcite and quartz, studied by a sequential extraction technique, shows that fracture sorption efficiently retards uranium transport in fractures. The most important phenomenon seems to be calcite formation (Figure 5 A). Uranium concentrations in calcite up to 1600 ppm have been measured (Suksi, 1990). Long retention time for uranium in calcite, determined by U-series disequilibrium measurements, have also been recognized (Suksi et al., 1990). The $^{234}U/^{238}U$ activity ratios of extracted phases suggest limited mixing of groundwaters in the study area. Also uranium deposition in different groundwater conditions as well as deposition at different times can be inferred (Figure 5 B).

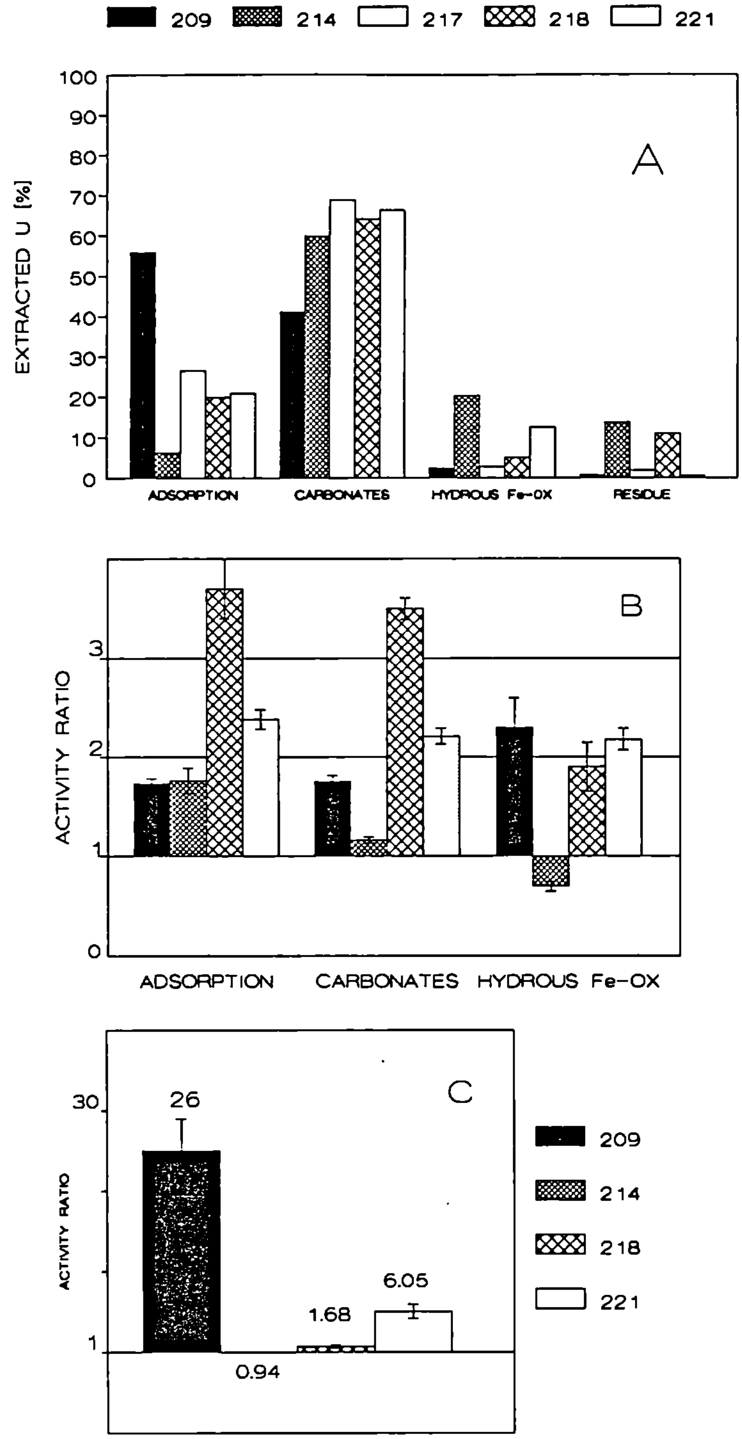

Figure 5. The occurrence of uranium and the $^{234}U/^{238}U$ activity ratios in fracture coatings studied by selective extractions:
A) distribution of uranium between different phases, B) $^{234}U/^{238}U$ activity ratios in extracted phases, C) $^{234}U/^{238}U$ activity ratios in residual phases left after the three preceding extractions.

Future studies

Various isotopical methods are used to clarify previous bedrock conditions; an important part of these studies deals with the dating and formation of geologically young calcites. In addition to the $^{230}Th/^{234}U$ dating method also $^{231}Pa/^{235}U$ method is introduced. The diffusion of uranium and other elements into the rock will be studied. The characterization of particulate matter in groundwater and studies on fracture mineralogy and alteration phenomena of uraninite in the Palmottu area are continued.

Planned studies concentrate on radionuclide migration both in the oxidizing and reducing part of the bedrock. A comprehensive part of the studies will be devoted to clarify the overall structural and present hydrological features of the area.

5. APPLICABILITY TO PERFORMANCE ASSESSMENTS

The strength of natural analogues from performance assessment point of view is, that it is often possible to study phenomena under relevant time and spatial scales. The weakness, on the other hand, is that the initial and boundary conditions of the analogues are often extremely difficult to determine. This makes quantitative interpretation often very difficult.

Natural analogue studies can thus be useful for performance assessments on three levels:

- quantitative validation of models, or directly applicable quantitative results
- qualitative validation of models to ensure, that e.g. no important mechanisms have been ignored
- spin off -results, that have no direct application in performance assessments as such, but which can be useful indirectly e.g. in contributing to the development of appropriate research methodology.

As an attempt to relate natural analogue studies to performance assessments of the Finnish disposal concept, a strongly simplified outline of its safety factors is presented in Figure 6. It can be seen that the Finnish natural analogue studies cover relevant areas of research, but e.g. radiolysis is still uncovered. It can also be seen in Figure 6 that natural analogues cannot alone solve all problems, since all subsystems of the disposal concept cannot be found in nature, but well-prepared lab and field experiments are needed, too.

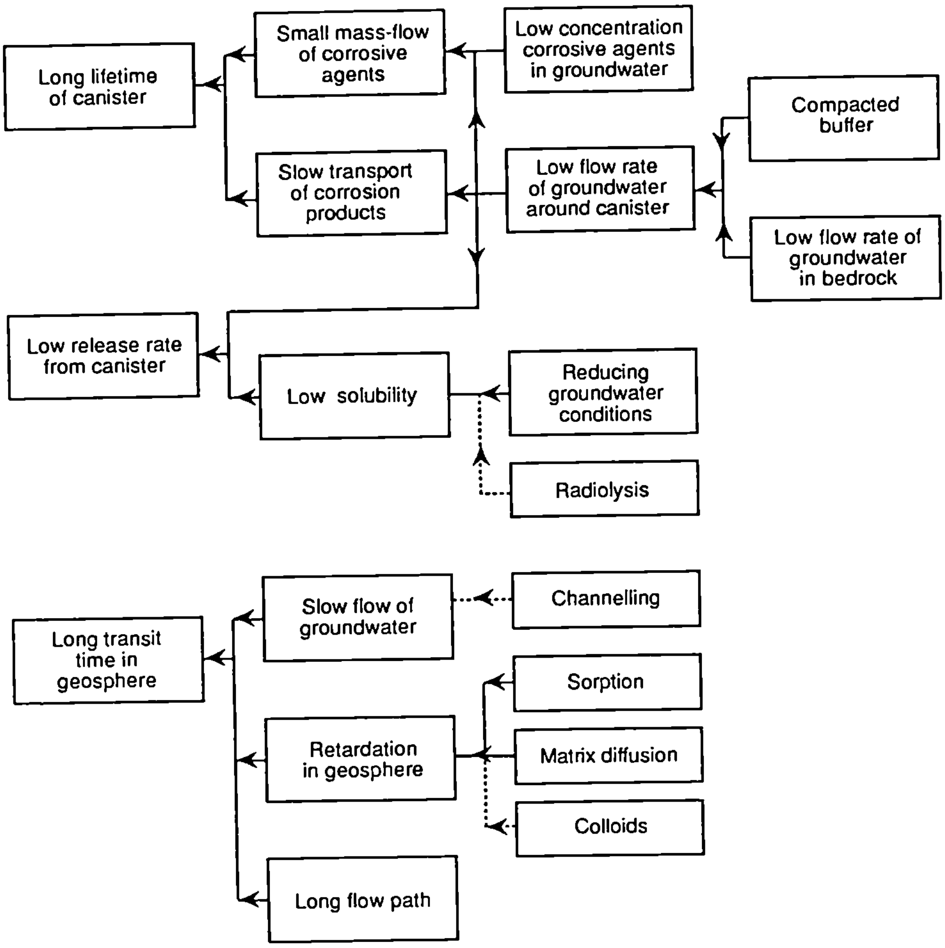

Figure 6. Safety factors of the Finnish geological disposal concept for spent fuel. Dotted lines represent potentially unfavourable effect to the overall safety.

Of the three Finnish natural analogue studies reviewed here, two seem to fall into the qualitative category, the third one is still at its beginning, so very little can at present be said about its final outcome.

The native copper study confirms qualitatively the long term stability of copper canister in Finnish bedrock.

Anion profile study has registered profiles clearly not in equilibrium in the scale of meters. Whether this has been caused by matrix diffusion or by strongly varying natural background is at present an open question since the study has not been concluded yet. The anion profile study has however proved that the quantitative interpretation of a natural analogue is not easy although the history of the Hästholmen site is exceptionally well known for a natural analogue.

Palmottu-project is at its beginning, so the conclusions are preliminary. Altogether 62 holes have been drilled at Palmottu, which enables detailed observations in and around the ore body, it also reduces the need for interpolations in interpreting the data. There are good possibilities to perform studies relevant to performance assessments, but a prerequisite to quantitative transport modelling is a reliable knowledge of the groundwater flow field. Flow field information is also needed in evaluating how representative the samples are, and in concentrating detailed measurements on strategic drill holes. The construction of the geohydrological model of Palmottu is under way.

6. CONCLUSIONS

Three Finnish natural analogue studies are reviewed and related to the Finnish disposal concept. Two of them fall into the qualitative category as seen from the viewpoint of applicability in performance assessments, the third one, Palmottu, is still at its beginning.

The existence of native copper in geohydrological conditions similar to geological environments in Finland supports qualitatively the long lasting stability of the copper canister.

The anion profiles measured at Hästholmen show disequilibrium in the scale of meters in rapakivi granite, matrix diffusion is one possible explanation. However, fitting of a simple diffusion model to the experimental results gives confusingly high diffusivities in the rock. Further efforts are under way to clarify the situation.

Phenomena and mechanisms responsible for the retardation of uranium have been identified at Palmottu. One important phenomenon is calcite formation. Long retention times for uranium has been shown. Some results of uranium analysis of groundwater indicate isolated groundwater flow regimes. The subsequent applicability (quantitative/qualitative) of the results in performance assessments depends heavily on how well the groundwater flow field can be determined.

The natural analogue studies reviewed cover relevant areas of research from performance assessment point of view, but e.g. radiolysis is still uncovered. Natural analogue studies cannot, however, alone solve all problems, because all subsystems of the disposal concept cannot be found in nature, but well-prepared lab and field experiments are needed, too.

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HYDROGEOCHEMICAL MODELLING OF THE NEEDLE'S EYE NATURAL ANALOGUE (SCOTLAND)

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INTRODUCTION.

The study of natural geochemical systems ("natural analogues") is useful in furthering the understanding of the processes that set in motion, transport and accumulate radionuclides in the area surrounding an underground waste disposal facility and it provides a means of testing the validity of coupled transport models and of the thermodynamic databases on which these models are founded.

The work summarized here concerns the modelling of uranium migration at the Needle's Eye site. This study is the result of a cooperation between the BGS (British Geological Survey), the SURRC (Scottish Universities Research and Reactor Centre) for the field aspects and the Centre d'Informatique Géologique (Ecole des Mines de Paris) for the modelling aspects. It was commissioned by the U.K. Department of the Environment, the French Commissariat à l'Energie Atomique (Institut de Protection et de Sûreté Nucléaire) and the Commission of European Communities (DG XII).

GEOLOGY AND URANIFEROUS DEPOSITS AT THE NEEDLE'S EYE SITE.

The study area is situated in the vicinity of the town of Dalbeattie (Kirkcudbrightshire) on the north bank of the Solway Firth (figure 1).

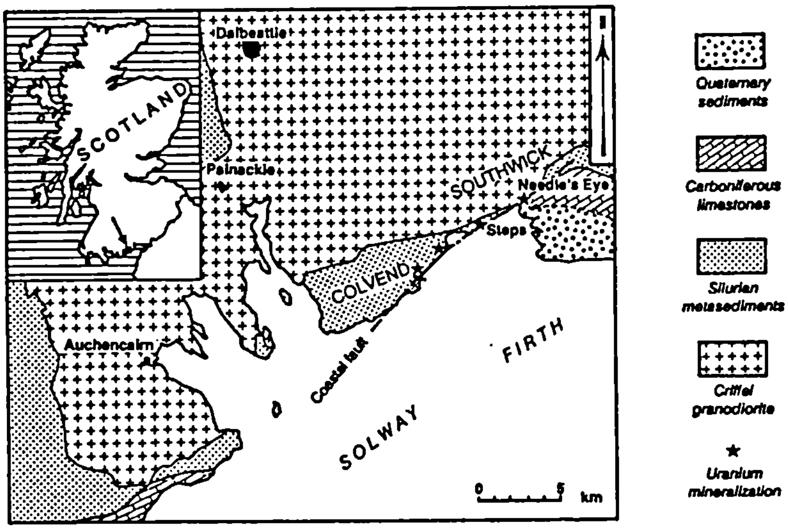

Figure 1. Location and geology of the Needle's Eye site (after Miller and Taylor, 1966).

The geology of this region was formed during the Palaeozoic, and consists mainly of silurian metasediments (hornfelses) intruded by Devonian granodiorites, in abnormal contact with carboniferous limestones through a major NE-SW hercynian fault. This contact is sealed by recent (-10,000 to the present) silty sediments laying at the bottom of a 40m-high paleocliff (figure 2).

Systematic uranium prospecting south of the Criffell batholith instigated by the Atomic Energy Division (1957-1961) brought to light signs of uranium in the vicinity of the coastal zone. In the Needle's Eye sector two large pitchblende-rich veins are visible in the cliff.

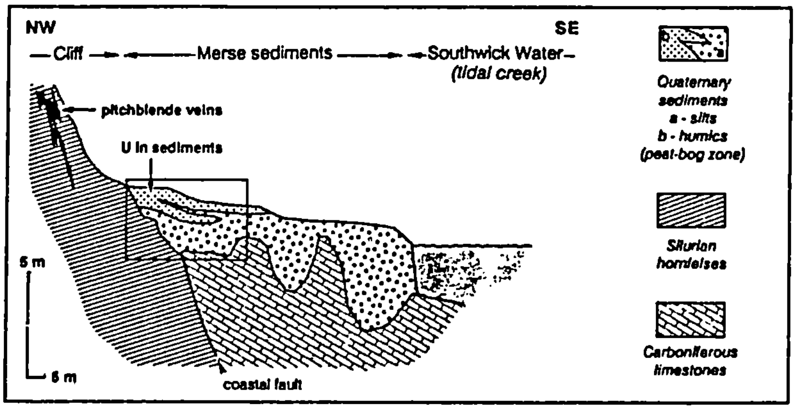

Figure 2. Uranium mineralization at Needle's Eye. Section following the BGS "line 18". The zone of application of the STELE code has been framed.

STUDY AREA.

Radiometric investigations of the sediments has shown evidences of uranium within the recent series, athough the precise reasons for its presence was not determined (primary deposits in the substratum, secondary in the sediments, etc.).

The most thoroughly studied zone consists of a band of recent sediments, 85 m long and around 50 m wide, from the cliff to a tidal channel (the Southwick Water) in a NW-SE direction. In this area, particularly on a given NW-SE profile ("line 18"), the BGS team has carried out a lot of stratified water samplings to determine the uranium distribution and the overall chemical composition of the water in the sediments.

HYDROGEOLOGICAL MODELLING.

Prior to the simulation of the uranium transport in the Needle's Eye site, it was necessary to describe the main features of the groundwater flow in the recent sediments. This was done in two stages, regional scale and local scale, given the lack of knowledge of the boundary conditions. The code used for these computations is the finite-elements METIS code [3].

The regional model is a 2-D NW-SE cross section (figure 3) including the Criffell granodiorite, the Silurian hornfelses, the Carboniferous limestones, the recent sedimentary deposits and the EW fault zone sealed by silts.

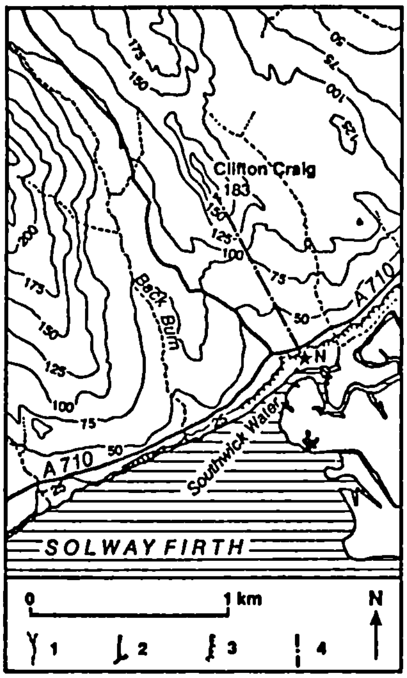

Figure 3. Topographic map of the Needle's Eye region (modified after Ordnance Survey sheet NX 85/95). Contours at 25 m interval, 1-streams ; 2-main roads ; 3-coastal cliff ; 4-modelled profile from Clifton Craig to Needle's Eye (N).

The local model is a detail of the preceding one, including all the Quaternary sediments found on line 18. In this series there are two main lithological facies, a humic facies which is abundant to the north (peatbog) and a silty facies, which takes up the rest of the domain.

Calculation shows that the flow is upwards in the peatbog (north of the fault) and mainly horizontal in the remaining area [4].

GEOCHEMICAL MODELLING.

The object of this work was to interpret the chemical data gathered by the BGS during the four measurement expeditions. One made use of the CHIMERE geochemical code which can calculate the saturation index of minerals potentially at equilibrium with the solutions.

On a qualitative point of view, the chemical measurements show that the uranium-rich waters are confined in the northern part of the sediments, in a one meter-thick zone near the hornfelses substratum. This statement, when added to the results of the hydrogeological local model leads to the conclusion that the sediments are contaminated by the leached pitchblende veins from the cliff.

On a quantitative aspect, the CHIMERE code shows that the more realistic uranium mineral at equilibrium with the solutions sampled in the sediments is uraninite (UO_2, a mineral close to pitchblende). The solubility limit of uraninite in the Needle's Eye waters goes from 10^{-7} mol/l at an Eh of +400 mV to 10^{-12} mol/l at an Eh of +200 mV [4].

HYDROGEOCHEMICAL MODELLING.

A first tentative interpretation of the observed dissolved uranium concentrations has been made with a K_d model, using the partition coefficients measured in the laboratory on peat samples from the site. This model does not account for the observed values [4].

The STELE hydrogeochemical model was then used in order to simulate the uraninite precipitation under reducing conditions in the sediments. A 100 ppb source term is fixed along the hornfelses substratum (Eh= 400 mV). A redox potential of 150 mV is fixed in the sediments.

This model shows that, provided a precipitation kinetics of 1 $mol.d^{-1}$, it is possible to reproduce almost exactly the observed stratification of the dissolved uranium concentrations in the northern area (figure 4 and table 1). Furthermore, the precipitated uraninite during a possible duration of the phenomenon ($\approx$ 5000 years, with regards to the average age of the sediments) falls in the range of the measured one (10 to 300 ppm [5]) [4].

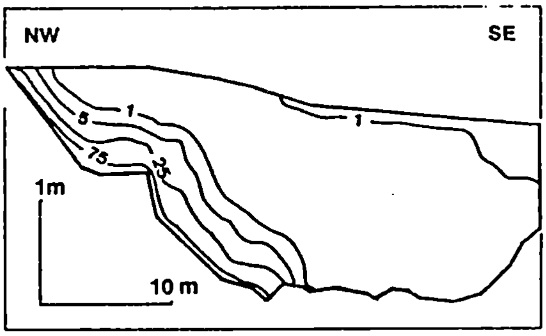

Figure 4. STELE code. Dissolved uranium at steady state in the northern area of the sediments (values in ppb).

Depth (cm)	Measured C (ppb)	Calculated C (ppb)
156	92,5	100
120	28,00	28,70
70	1,7	1,98
40	1,3	0,18

Table 1. STELE code. Comparison between measured and calculated uranium concentrations in piezometer 18,+20.

In conclusion, the model of uraninite precipitation under the reducing conditions within the quaternary sediments accounts reasonably for the observed uranium concentrations, both in the liquid and the solid samples collected at the Needle's Eye site. This model goes farther than a K_d model towards an understanding of the uranium transfer processes. However, this work has to be enriched by more thorough geochemical investigations in order to see whether the transport model has to be amended by the addition of other competiting geochemical mechanisms.

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SOME ASPECTS OF NATURAL ANALOGUE STUDIES FOR ASSESSMENT OF LONG-TERM DURABILITY OF ENGINEERED BARRIER MATERIALS

— RECENT ACTIVITIES AT PNC TOKAI, JAPAN —

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SUMMARY

This paper contains an overview of analogue studies for the assessment of long-term durability of engineered barrier materials at PNC Tokai.

Materials of young age and with simple history are the most suitable for study as: 1) properties of the materials tend to deteriorate over longer historical time intervals; and 2) detailed quantitative data on time intervals and environmental conditions are more likely to be available. The following materials and their alteration phenomena were selected: 1) weathering alteration of basaltic glass (as vitrified waste form), 2) corrosion of iron in soil (as overpack), 3) illitization of smectite associated with contact metamorphism (as buffer material), 4) alteration of cement (as buffer or backfill material).

1. Weathering alteration of basaltic glass: Basaltic glasses, from the Fuji and the Izu-Ohshima pyroclastic fall deposits were studied. The observations were made: 1) Climatological conditions have not varied significantly during the last three thousand years. Therefore, values for temperature, amount, and chemistry of ground water are quantified. 2) The cases studied could be regarded as leaching experiments in groundwater, using mass balances in water-glass interaction. 3) Although the groundwater is of Ca(Mg)-HCO_3 type in the Fuji area and of Na-Cl type in the Izu-Ohshima, similar alteration ratios ($2 \sim 3\mu$m/1000yr) were obtained.

2. Corrosion of iron in soil: Industrial materials, such as gas/water service pipes of carbon steel or cast iron embedded in soil for 20 ~ 110 years, were selected for an analogue study of corrosion of iron in bentonite. The maximum corrosion rates obtained so far fall in the range of 0.04 ~ 0.09 mm/yr.

3. Illitization of smectite associated with contact metamorphism: In the Murakami bentonite deposit in central Japan, lateral variation of smectite to smectite/illite mixed-layer minerals are found in the aureole of the rhyolite intrusion body. Conversion of ~~smectite~~ to the mixed-layer mineral composed of 40% illite was found to have occurred in a period of 2.4 Ma over a temperature range of above 240 (±50) ℃ to 105 ℃.

4. Alteration of cement: Concrete components of fabrications, such as estuary walls, with a known age were studied. Chemical alteration of the cement were detected to a depth of few centimeters by EPMA, SEM, TEM and XRD.

5. Framework of our analogue studies: Our natural analogue programme has three components: 1) investgation of alteration phenomena, 2) examination of environmental conditions, 3) support experiments. The support experiments are an essential part of our study in order to enhance the wider applicability of the natural analogue.

1. INTRODUCTION

1.1 COMPONENTS OF ENGINEERED BARRIERS

The Components, candidate materials, and functions of various types of engineered barriers are as follows:

Components	Candidate materials	Function expected
• Vitrified waste	• Borosilicate glass	• Restricts release*
• Overpack	• Carbon steel or Cast iron	• Retards water penetration * • Provides favourable chemistry *
• Buffer materials	• Bentonite	• Restricts water penetration * • Delays commencement of release* • Restricts radionuclides release *
• Backfill materials	• Concrete (Cement)	• Minimizes water access to package† • Alters groundwater chemistry † • Retards solute transport †

(* :NAGRA [1985], † :Chapman et al [1987])

As a part of the study on engineered barrier materials and systems for geological disposal of radioactive waste in Japan, analogue studies for the assessment of long-term durability of engineered barrier materials are conducted at PNC Tokai Works. This paper describes the state-of-the-art on the studies, specifying their main purposes and framework, and demonstrating our emphasis on natural materials. The results obtained to date will be summarized. Some parts of studies on natural glass and bentonite were already presented at the MRS Symposium (Arai et al., 1988; and Kamei et al., 1989), although revised and expanded data are shown here.

1.2 DEFINITION OF "NATURAL ANALOGUE"

One of the most critical aspects in the evaluation of the durability of candidate materials for engineered barriers is the extrapolation of the results of short-term experiments over a long time scale. Natural analogues currently provide the only means by which such extrapolated long-term behaviour can be confirmed.

The term "natural analogue" can be defined as "natural phenomena which resemble those assumed in geological disposal scenarios". The selection of an appropriate natural analogue is the key issue which will determine whether the natural analogue study will be successful.

1.3 PROPERTIES OF NATURAL ANALOGUE

First, consideration is given to the properties of the natural analogues. In order to extrapolate the results of short-term experiments to the long-term, it is desirable that the natural phenomena can be individually and quantitatively described in terms of three constituents: 1) starting materials, 2) environmental conditions (including time scale), and 3) results. These are the three normal constituents of all "experiments".

However, there are some intrinsic difficulties in regarding such phenomena as experiments. Most naturally occurring materials, from which an relevant analogue must be selected, have complicated histories resulting the overprint of different processes, as shown in Table 1.

Table 1 Comparison between laboratory experiments and natural phenomena

	Laboratory Experiments	Natural Phenomena
(1) Materials	Candidates	Analogue
① Number	Many	Solitary, few
(2) Environmental (Experimental) Condition	Simple, Uniform Constant, Controlled Common. Small Scale	Complicated Variable Individual Large Scale
(3) Period	Short-term	Long-term
(4) Results	Independent variables Discrimination among conditions is possible	Overprinting of factors Restoration is difficult

Secondly, geological and historical records are often incomplete, and errors in the determination of time scale and environmental conditions are not small. Although such disadvantages differ case to case and sample to sample, as materials age, their histories generally become more complicated; the factors with which alteration phenomena were related become overlapped, and quality and quantity of available data decreases. Thus, estimation from present observations becomes virtually impossible with very old samples (Figure 1).

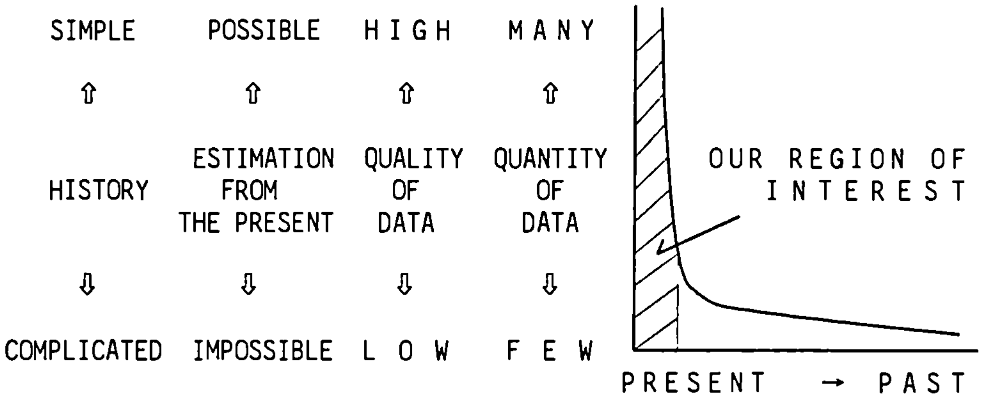

Fig. 1 Properties of historical materials

1.4 SELECTION OF SUBJECTS FOR THE STUDIES

Cases of younger age and simple process, therefore, are regarded as more suitable subjects for the studies, as quantitative data on time and environmental conditions are probably available. Many previous analogue studies consisted of descriptions of the results of natural experiments without incorporating data on well-defined environmental conditions.

We selected subjects for the analogue studies according to the following criteria: 1) analogy of materials with candidates, 2) analogy of environmental conditions with simulated repository conditions, 3) simplicity and availability on environmental conditions, and 4) availability of chronological data. Table 2 shows the subjects of our analogue studies on engineered barriered materials.

Table 2 The subjects of our analogue studies on engineered barrier materials

Engineered Barriers	Candidate Material	Assummed phenomena in Repository Conditions	Analogue Phenomena in Analogous Conditions
1.Waste Form	Boro-silicate Glass	Leaching of Waste Borosilicate Glass with Groundwater	Weathering Alteration of Basaltic Glass with Goundwater
2.Overpack	Carbon Steel	Corrosion of carbon steel in Bentonite	Corrosion of Iron in Soil
3.Buffer Materials	Compacted Bentonite	Illitization of Smectite in Bentonite	Illitization with Contact Metamorphism
4.Backfill Materials	Concrete (Cement)	Alteration of cement with Groundwater	Alteration of Cement with Groundwater

2. Weathering alteration of basaltic glass

2.1 SCOPE OF STUDIES

Many analogue studies of the alteration of natural glasses indicate that the alteration rates at low temperatures of natural glasses vary from 0.001μm/1000 yr to 30 μm/1000 yr (Hekinian et al. 1975; Bryan et al. 1977; Allen 1982; Lutze et al. 1985 & 1987; Grambow et al. 1986; Ewing et al. 1987; Jercinovic et al. 1988). This variation is interpreted as the result of variations in environmental conditions. However, few detailed studies on environmental conditions have been reported.

Described below are the effects of alteration by weathering of basaltic glasses with well established environmental conditions and ages. The alteration is a long-term leach test carried out by nature with rainwater as the leachant and groundwater as the leachate. The young-aged (280 ~ 2800 years) samples were selected to investigate environmental conditions during alteration based on present meteorological data.

Samples

Volcanic glasses constituting scoria of pyroclastic fall deposits were studied. Scoria samples were collected at the foot of the Fuji and Izu-Ohshima volcanoes, on both of which the stratigraphy and chronology of pyroclastic fall deposits have been studied in detail.

The samples collected were Houei Scoria (HS, 280 years ago) and Zunazawa Scoria (ZS, 2800 years) from the Fuji, and N1 (880 years) and N4 Scoria (1240 years) from the Izu-Ohshima volcano.

All of the scoria samples contained pore water, and spring water was found about 2.5 m below the Zunazawa Scoria bed.

Methods

Glass compositions were determined by Electron Probe Microanalyser (EPMA). Alteration layers were studied by optical microscope, EPMA and Scanning Electron Microprobe (SEM). The thickness of alteration layers was measured from SEM photos of the sections oriented nearly perpendicular to the layers.

In the field, the pH and Eh of the spring water were measured by portable meters. The spring water was filtrated through a 0.45μm filter and the filtrate was analyzed by absorption spectrophotometry, flame spectrometry and atomic absorption spectrometry.

2.2 RESULTS

The chemical compositions of the glasses are shown in Table 3. These are within the range of basalts.

Table 3 Chemical compositions of glasses.

Sample	Oxide (wt%)								
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3*	MgO	CaO	Na_2O	K_2O	Total
Fuji									
HS	52.9	2.3	12.1	16.5	3.9	8.5	1.8	1.2	99.2
ZS	50.7	1.6	15.0	13.8	4.9	8.8	2.9	0.9	98.6
Izu-Ohshima									
N1	53.7	1.4	13.0	15.6	3.4	8.8	2.3	0.5	96.9
N4	53.0	1.4	13.1	15.3	4.4	8.4	3.9	0.5	98.6

*: Total Fe as Fe_2O_3

Alteration layer

The alteration layer is optically isotropic and X-ray amorphous. The surface form of the alteration layer of the HS is grainy and that of ZS, N1, and N4 is flaky.

Despite the difference in morphology, the chemical composition of the alteration layer of the Houei Scoria is similar to that of the Zunazawa Scoria. The morphology of the alteration layers of both scoria is strikingly similar to that observed on the surface of experimentally altered borosilicate glasses (Hirose, unpublished data). Alteration layer thicknesses are summarized in Table 5. The elemental concentrations in the alteration layer are characterized by greater depletion of Mg, Ca, Na, and K, as compared to Si, Al, Fe, and Ti.

Table 4. Chemistry of pore water, spring water and rainwater.

Sample	Chemical composition (mg/l)									pH	Eh (mV)
	Na	K	Ca	Mg	Fe	HCO_3	SO_4	Cl	SiO_2		
Fuji											
HS P.W.	4.4	1.7	5.3	1.3	—	24	6.5	4.1	34	—	—
ZS P.W.	8.4	3.3	4.6	1.3	5.0	35	6.4	4.3	218	—	—
S.W.	5.0	1.4	8.9	6.9	2.9	67	4.4	2.6	41	7.0	178
Izu-Ohshima											
N1 P.W.	78	2.9	27	12	3.2	7.6	27	176	52	(6.0)	—
N4 P.W.	86	3.7	40	15	4.0	6.1	26	222	48	(6.0)	—
Rain water*	1.1	0.3	0.4	1.0	0.2	—	1.5	1.1	0.8	—	—

P.W. = Pore Water; S.W. = Spring water, * after Sugawara (1968)

Water chemistry

The chemistry of the pore and spring water is listed in Table 4, together with the average of rainwater in Japan (Sugawara, 1968). The elemental concentrations in ZS pore water are higher than those in HS pore water. This implies that elemental concentration in groundwater increases with depth.

2.3 DISCUSSION

Environmental Conditions

Analyses of paleo-sea level variations (Sugimura, 1977) and paleo-climatological data (Yamamoto, 1980; and Maejima, 1984), indicate that the climatic conditions in Japan have not varied significantly for the last 2800 years. Therefore, the temperature and the water supply rate are estimated from meteorological data such as mean annual temperature, annual rainfall, and evapotranspiration. The samples were situated in the unsaturated zone; accordingly, percolating meteoric water is the only source of pore water. The pore water flows downward in the deposits and dissolves the components of scoria. This natural phenomenon can be regarded as a leach test being constantly renewed fresh rainwater.

Alteration Rate

In natural alteration systems, it is generally difficult to know the exposure age of a sample, that is, the time that the glass has actually been in contact with water (Jercinovic et al., 1988). The exposure ages of the samples in this study are equivalent to the samples ages as their surfaces were always in wet conditions and were always in contact with renewed pore water.

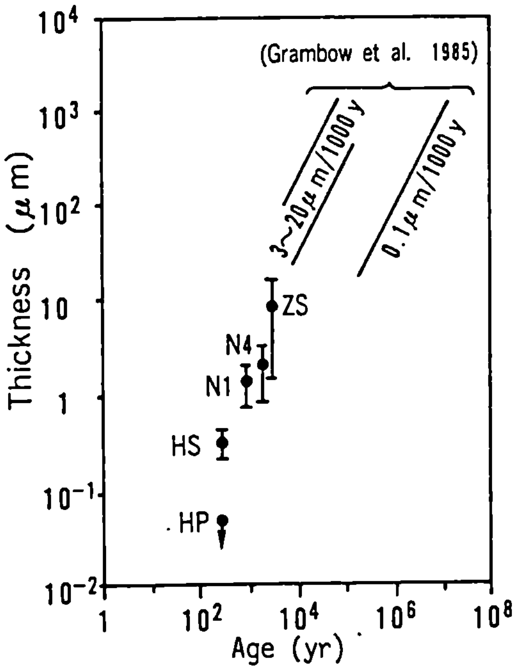

Fig. 2 The relation between age of samples and thickness of alteration layer

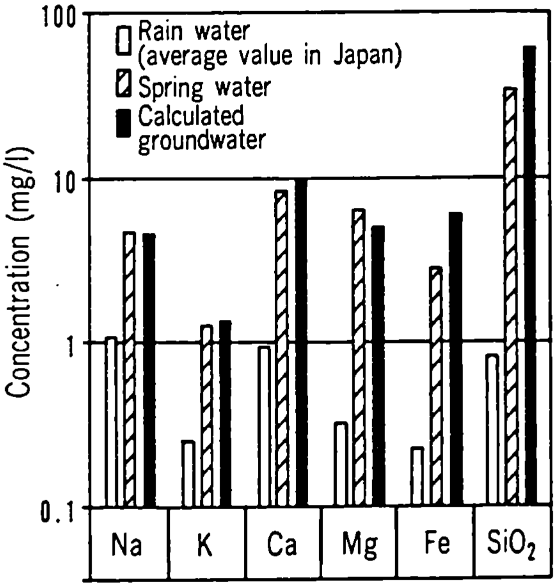

Fig. 3 The comparison between elemental concentrations of spring water and calculated groundwater

The relation between alteration layer thickness and age is shown in Figure 2. The two kinds of alteration rates, the forward rate of alteration (3 ~ 20 μm/1000 yr, under silica-unsaturated conditions) and the final rate of alteration (0.1 μm/1000yr, under silica-saturated conditions) by Grambow et al.(1985), are also shown in Figure 2. The alteration rates estimated in this study are near or below the forward rate of alteration.

Mass Balance Between Alteration Layer and Spring Water

Spring water can be regarded as the leachate. In order to discuss the leaching behaviour of glass, it is necessary to clarify the relation between the elemental concentration in the leachate and the elemental loss from the alteration layer. Elemental concentrations in groundwater have previously examined (Arai et al., 1989) and the results indicate that the calculated composition of groundwater is in fair agreement with the composition of spring water (Figure 3). The discrepancies in the concentrations of Fe and SiO_2 can be explained by the precipitation of iron hydroxides and silica gel respectively among scoria grains.

Table 5 Summary on alteration behaviour of volcanic glasses and their environmental conditions

(1) MATERIALS STUDIED	FUJI			IZU-OHSHIMA	
	HP	HS	ZS	N1	N4
(2) GLASS COMPOSITION[SiO_2wt%]	64	53	51	54	53
(3) ENVIRONMENTAL CONDITIONS					
①TEMPERATURE(℃)	14			15	
②WATER CHEMISTRY	Ca(Mg) - HCO_3 type			Na - Cl type	
③WATER SUPPLY RATE(ℓ /㎠ /yr)	0.20			0.21	
(4) PERIOD (yr)	280	280	2800	880	1240
(5) RESULTS					
①ALTERATION RATE(μm/1000yr)	< 0.2	1.6	3.1	1.7	1.8
[Alteration Layer Thickness: μm]	< 0.05	0.44	8.8	1.5	2.2
②ALTERATION PRODUCTS					
• Amorphous Materials	N.D.	○	○	○	○
• Goethite	N.D.	○	○	○	○
• Smectite	N.D.	×	○	○	○

N.D. : Not Determined, ○ : Present, × : Absent

2.4 CONCLUSION

1) It was possible to determine the alteration behaviour of volcanic glasses from three experimental constituents: 1) starting materials, 2) environmental conditions and time scale, and 3) results (Table 5).

2) Calculation of the mass balance between the elements depleted from the glasses and the chemical composition of groundwater permitted us to regard the cases studied as experiments in the leaching of glasses by groundwater.

3) The natural alteration products of the volcanic glasses were very similar to those of laboratory experiments with simulated waste glasses.

4) Although the ground water is Ca(Mg)-HCO_3 type in the Fuji area, and of Na-Cl type in the Izu-Ohshima area, similar alteration rates (2 ~ 3 μm/1000 yr) were obtained.

3. CORROSION OF IRON IN SOIL

Industrial materials such as water service pipes, were studied for the following reasons: 1) iron or steel is one of the candidate materials for waste package, 2) soil environment is probably similar to the bentonite fill environment, 3) samplavailability, and 4) chronology and environmental data are fairly assessable in ccomparison to those of archeological artifacts. One of the purposes of this analogue study is to validate whether the results of corrosion rates and models derived from the results of laboratory experiments can be extrapolated to a few tens of years (Figure 4).

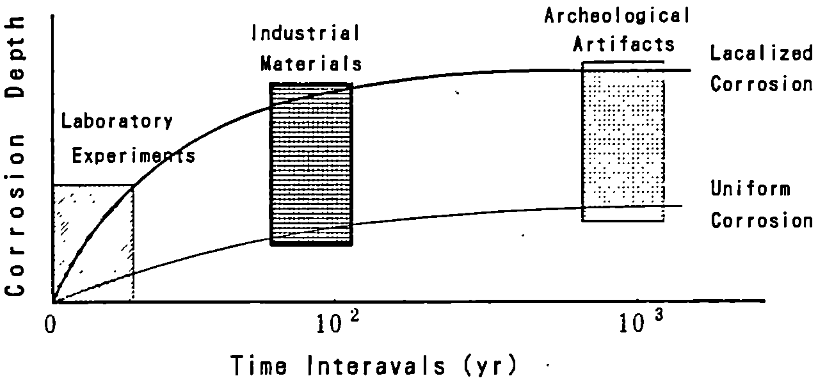

Fig. 4 The relation between the subjects for studies on corrosion of iron and their time interval

The samples studied were gas or water service pipes, composed of cast iron or carbon steel. The soil or clay adjacent to the pipe was examined in order to avoid the influence of the macro-cell effect. The corrosivities of the soil environment at each site were estimated as not being very severe from the viewpoint of both electrochemical and chemical characteristics of the soil. Corrosion rates were derived from the measurements of the thickness of the pipe, and chemical composition of the material were determined. The corrosion products were identified with X-ray diffraction (XRD). The results obtained to date are shown in Figure 5 and Table 6.

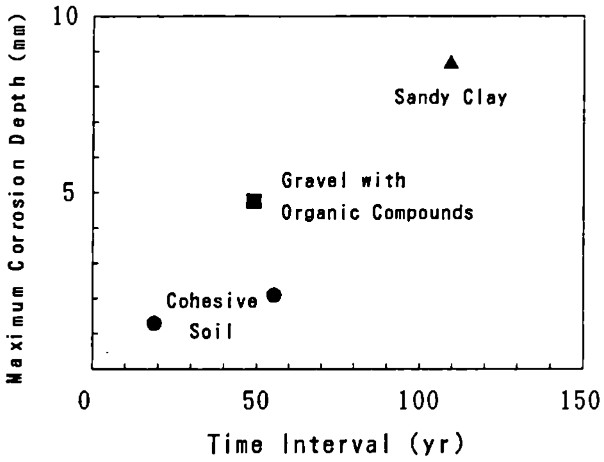

Fig. 5 Maximum corrosion depth as a function of time intervals

In conclusion, the maximum corrosion rates of cast iron and carbon steel embedded in soils were estimated in the range of 0.04~0.09 mm/yr. Corrosion of industrials materials in soil is a useful analogue and further studies are planned.

Table 6 Corrosion behaviour of iron in soil

(1)MATERIALS STUDIED				
① Site	Yokohama	Nagasaki	Tokyo	Tokyo
② Sample	Gas S.P.	Water S.P.	Water S.P.	Water S.P.
③ Material	Cast Iron	Carbon Steel	Cast Iron	Cast Iron
(2)ENVIRONMENTAL CONDITIONS	Sandy Clay	Gravel with Org. Comp.	Cohesive Soil	Cohesive Soil
(3)PERIOD (yr)	110	50	56	20
(4)RESULTS				
① CORROSION RATE(mm/yr)				
Uniform Corrosion	0.03	0.01	N.D.	N.D.
Pitting Corrosion	0.08	0.09	0.04	0.06
② CORROSION PRODUCTS	$FeCO_3$	Not identified	$FeCO_3$, α-FeO(OH)	$FeCO_3$, α-FeO(OH)

S.P. = Service Pipe; Org. Comp. = Organic Compounds

4 . ILLITIZATION WITH CONTACT METAMORPHISM

4.1 SCOPE OF STUDIES

The research on illitization of smectite in the natural environment affords indispensable information on the long-term durability of bentonite.

Geological processes associated with smectite-illite conversion can be classified as follows:
1) Diagenesis, 2) Regional metamorphism, 3) Contact(or thermal) metamorphism,

4) Hydrothermal alteration

Among theses, contact metamorphism has been selected as being a suitable analogue because of the prevailing temperature and the water/rock ratio. Furthermore, a study of contact metamorphism has potentiality to give clear-cut data on the reaction term and the thermal conditions of illitization of smectite, provided that: 1) the bentonite bed is distributed, and 2) simple history and simple geology can be recognized.

One such case of contact metamorphism is the Murakami bentonite deposit in central Japan, where a homogeneous bentonite bed and rhyolitic intrusive rock are present. Geological, petrological and geochronological studies have already been presented at the MRS symposium in Boston, 1989 (Kamei et al. 1990), so only a brief description of this deposit is given below:

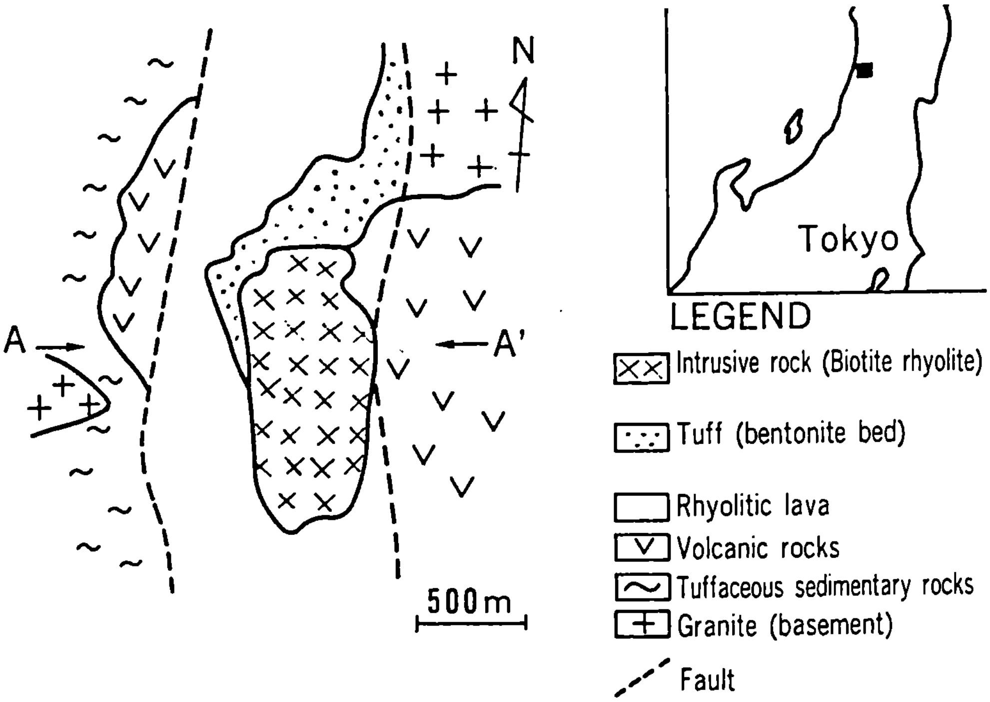

Fig. 6 Geological map of the Murakami deposit

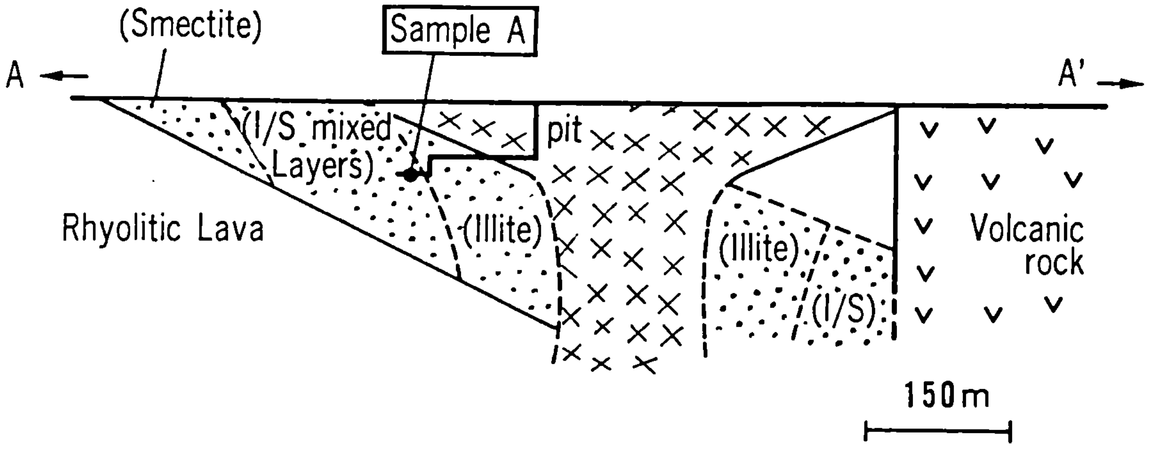

Fig. 7 An idealized geological section of the Murakami deposit

Geology

A geological map and an idealized section of the Murakami deposit area are shown in Figure 6 and 7, respectively. Rhyolitic lava and tuff are distributed in a graven with a width of approximately one kilometer. The reported age of deposition of this unit ranges from 18 to 14 Ma (Muramatsu, 1988). The tuff is regarded as being deposited in a marine environment, and was converted into bentonite possibly due to diagenetic reaction. Subsequent intrusions of biotite rhyolite are found in the bentonite bed. The contact between the intrusive rock and the tuff dips about 30° near the surface of the ground, and the intrusive rock body is assumed to form a funnel with a diameter of less than 200 meters (Figure 7).

Samples

Sample A was collected from a point 30 meters distant from the contact between the intrusive body and the bentonite bed. X-ray diffraction showed that sample A contained illite-smectite mixed layers with an illite ratio of about 40 %.

4.2 RESULTS

Thermal History

The cooling rate of the intrusive rock was determined from combining radiometric mineral ages and each closure temperature. The cooling rate of sample A was estimated by the "TRUMP" thermal analysis code. The results are shown in Figure 8. The cooling rates of the intrusive rock and of sample A were 70 ℃/Ma, and 60 ℃/Ma, respectively. (Figure 8 and the values for cooling rates are newly revised, therefore those reported in the MRS Proceedings (Kamei et al. 1990), should be ignored.)

The Illitization Period

In the Murakami deposit area, a minimum temperature of illitization is regarded as 105℃, because this was the temperature estimate made by Oda et al. (1985) for the appearance of illite-smectite mixed layers in Japanese oil fields, of which the Murakami deposit form a part. In the vicinity where sample A was collected, the temperature at 6.4 Ma was presumed to be 240 ±50℃. Therefore, a period of about 2.4 Ma was required to cool these rocks from 240 to 105℃.

In short, smectite was converted into illite-smectite mixed layers, in which the illite ratio is approximately 40 %, in the period of more than 2.4 Ma.

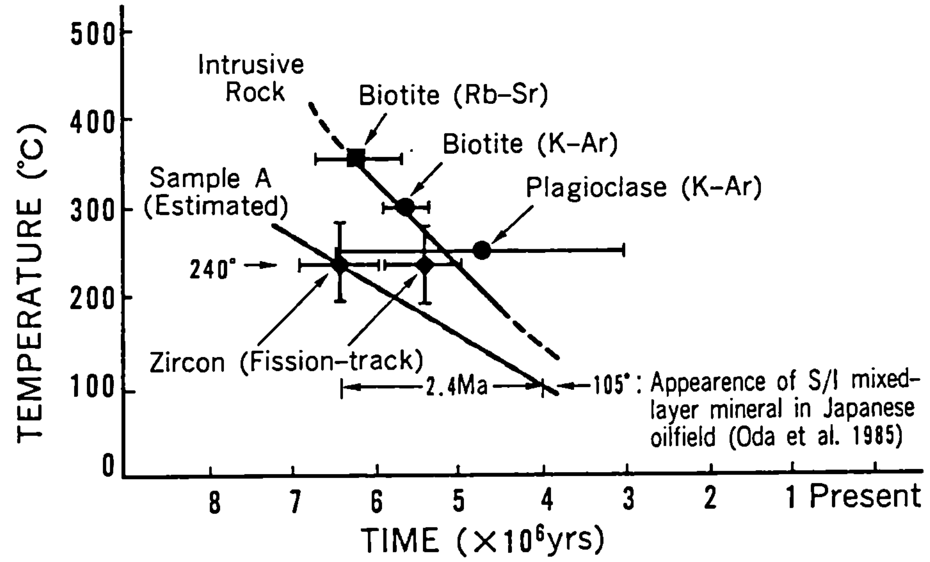

Fig. 8 Thermal history of intrusive body and sample A

Water Chemistry

The chemical composition of the rocks distributed in the Murakami area is mostly rhyolitic, and the tuff, now converted into bentonite bed, is of marine origin. The geological evidence leads to the idea that the chemistry of the water related to illitization was very similar to that of seawater after it was modified by interaction with rocks of rhyolitic composition.

The hydrogen isotopic composition (D/H) of water, in the form of hydroxyl groups, in the illite and the smectite-illite mixed layers, were measured, and from this an assessment of the water involved in illitization was made. The results supported the idea noted above.

Provisional Calculation of Activation Energy

The activation energy for illitization at the Murakami deposit was provisionally calculated on the basis of the estimated thermal history. The calculation procedure was already described in Kamei et al. (1990). Using the revised cooling rate of 60 ℃/Ma and a period of 2.4 Ma. the activation energy is approximately 27 kcal/mol. This value is close to that obtained by Roberson & Lahann(1981) of approximately 30 kcal/mol. The water used for their experiments contained 400 ppm K^+ and 9400 ppm Na^+, the chemistry of seawater. A similar water chemistry can be inferred at Murakami.

Table 7 Summary of a study on illitization of smectite associated contact metamorphism— A case study at the Murakami deposit

(1) Material	Smectite in marine sediment
(2) Environment ① Water chemistry ② Temperature	 Modified seawater > 240 ℃ ~ 105 ℃
(3) Period	2.4 Ma
(4) Result	I/S mixed layers mineral (Illite;approximate 40%)
(5) Activation energy	Approximate 27 kcal/mol

4.3 CONCLUSION

Once again returning to the three-part concept of starting materials, environmental and chronological conditions, and results, it was possible to describe the illitization of smectite associated with contact metamorphism in terms of 1) material studied, 2) environment, 3) period, and 4) results (Table 7). A more precise estimation of activation energy is possible through an estimation of the overall thermal history during contact metamorphism, using a thermal analysis code. This work is in progress.

5. ALTERATION OF CEMENT

Concrete components such as tunnels or estuary walls with known ages were studied. Environmental conditions such as temperature, surrounding materials, water content, and water chemistry ware either measured or estimated. The alteration of cement materials has been analyzed by EPMA, SEM, TEM(Transmission Electron Microscopy), and XRD. Results obtained to date are shown in Table 8.

The following alteration features of cement materials was able to be traced:

(1) Decrease in pH of pore water,
(2) Decrease of CaO/SiO_2 ratio of C-S-H gel,
(3) Partial dissolution of C-S-H gel,
(4) Formation of $CaCO_3$,
(5) Permeation of Cl, resulting in formation of Friedel'Salt.
(6) Dissolution of Calcium hydroxide,
(7) Dissolution of Calcium which cause dissolution of $CaCO_3$,

Such alteration phenomena were detected within a range of a few centimeters. Further studies are necessary to permit any definite conclusions.

Table 8. Alteration behaviour of cement fabrics

(1) MATERIALS STUDIED		
① SITE	Kanagawa	Yokohama
② SAMPLE MATERIALS	Concrete of Tunnel Wall	Concrete of Estuary Wall
(2) ENVIRONMENT		
① Temperature	13 ℃	15 ℃
② Surrounding Materials	Lapilli tuff	Soil
③ Water Content	40 %	33 %
④ Water Chemistry	Ca - $NO_3(HCO_3)$	Na - Cl
(3) PERIOD (yr)	67	61
(4) RESULTS OF ALTERATION	Ca depletion <few mm	Cl permeation >10 cm $CaCO_3$ formation >8 cm $CaCO_3$ dissolution >5 cm

Table 9 The present state of PNC analogue studies on engineered barrier Materials

Barrier Components (Candidate Materials)	Materials and Mode of Occurrence	Period (yr)	Estimation of Period	Estimation of Environmental Conditions
Waste Form (Borosilicate glass)	Scoria (Pyroclastic Fall Deposit)	$10^2 \sim 10^4$	Tephrochronology	From Recent Climatological Conditions
Buffer (Compacted Bentonite)	Contact Metamorphosed (Natural) Bentonite	$10^6 \sim 10^7$	Radiometric Age Determination	Closure Temperature of Radiometric Ages Geological and Geochemical Data
Overpack (Carbon Steel)	Industrial Materials (Pipe)	$10^1 \sim 10^2$	Documents	From Present Embedded Conditions
Backfill (Concrete)	Industrial Materials (Components of Fabrics)	$10^1 \sim 10^2$	Documents	From Present Embedded Conditions

6. SUMMARY AND FUTURE PROSPECTS

Table 9 summarizes the present state of PNC analogue studies on engineered barrier materials, and Figure 9 shows the framework of our analogue studies.

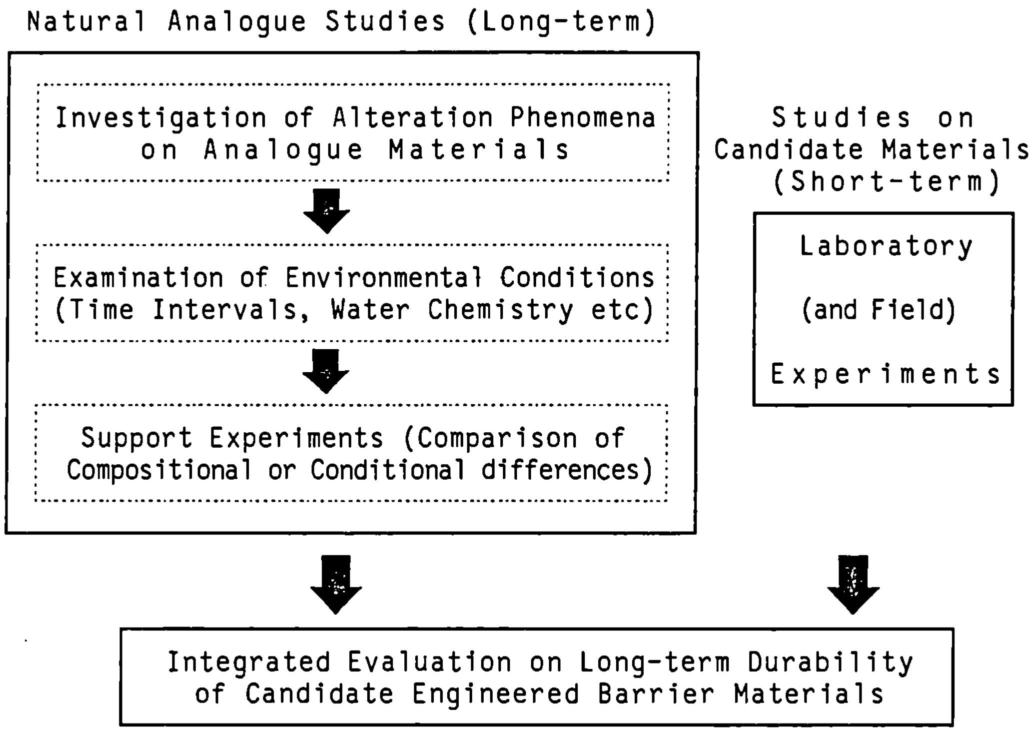

Fig. 9 Framework of analogue studies on engineered barrier materials

Our natural analogue studies have three components:

1) investigation of alteration phenomena of analogue materials,
2) examination of environmental conditions (time intervals, water chemistry etc),
3) support experiments

The validity of the analogue study is determined by the selection of alteration phenomena of analogue materials out of various natural phenomena acting on historical materials from the point of view of best analogical fit.

An examination of environmental conditions occupies an inevitable part of the study. Time intervals, prevailing temperature, and water chemistry related to the alteration are key items.

Support experiments are indispensable to the study in order to enhance the wider applicability of the natural analogue. Comparison of differences in composition or condition is the key issue for laboratory support experiments. Such experiments for the comparison of compositional differences between basaltic glasses and candidate waste glass have already started, and the results to date indicate that there is no significant recognizable difference in the leaching rates.

From a combination of the natural analogue studies outlined above and laboratory experiments on the candidate materials, an integrated evaluation of the long-tem durability of candidate engineered barrier materials can be conducted.

ACKNOWLEDGMENTS

We are sincerely grateful to Prof. H. Machida, Dr. K. Hakamada, Dr. K. Marumo and Mr. M. Sato for their useful suggestions for obtaining samples, to Prof. K. Suzuki for provision of standard samples for analysis by EPMA, to Mr. Y. Sakuramoto for valuable discussions, to Mr. T. Teshima and Mr. J. Yamagata for their preparation of Tables and Figures, to Prof. Y. Kuroda and Mr. Y. Suzuki for hydrogen isotope determinations, to Mr. H. Takano for field survey, and Dr. M. Apted and Dr. G. Davidson for their heipful editing.

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1) Department of Glass Industry, Ohsaka Industry Laboratory, in the laboratory leaching experiments of both borosilicate and basaltic glassess;
2) Dr. K. Tamada, Corrosion Protection Laboratory, NKK Corporation, in charge of corrosion studies on carbon steel pipe in soil environments;
3) Laboratory of Clay Mineralogy, Jyoetsu University of Education, especially Professor T. Watanabe as technical and scientific advisor concerning the illitization study;
4) A cooperative group of companies consisting of Kajima Corporation, Shimizu Construction Co. Ltd, Taisei Corporation, and Ohbayashi Corporation, in the sampling of concrete materials and in acquisition of data on environmental conditions;
5) Laboratory of Cement Mineralogy, Nagoya Institute of Technology, especially Professor K. Suzuki as technical advisor concerning hydration of cement materials;

to all of these organizations and people we are much indebted.

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A NETHERLANDS NATURAL ANALOGUE

Uranium-enriched nodules in a brackish sandy aquifer

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History

In drilling operations carried out by the State Water Board on the island of Schouwen in the south-west of The Netherlands (Fig. 1) /1/, during 1968 and 1969, unusual high peaks were found in the gamma radiation measurements. These peaks appeared to be due to the presence of three layers of phosphorite nodules, which were enriched in uranium /2/. To obtain some idea of the extension of these layers, the State Geological Survey re-examined the data of drillings in a larger area. Phosphorite nodules were recognized in several drilling samples on the islands of Walcheren /3/ and Beveland /4/ in the south-west of The Netherlands, but were generally not described as such. The uranium content of the nodules, however, appeared to be too low for economic exploitation of uranium to be considered.

Phosphorite nodules

The first phosphorite layer occurs at the top of the Antwerp Sands (M. Miocene), the second layer lies at the base of the Deurne Sands (U. Miocene), and the third layer is found at the base of the Kattendijk Sands (L. Pliocene) (Figs. 2-6). The size of the phosphorite nodules ranges from 0.5 to 10 cm. The nodules are composed of light-green glauconite globules and rounded quartz grains (with subordinately some feldspar grains), embedded in a brown cryptocrystalline matrix composed of apatite. In the matrix tiny sericite flakes and some ore minerals are present. The accessory minerals include chlorite, zircon, garnet, epidote, titanite, hornblende, and probably collophane and francolite. The uranium appears to be bound to apatite, which accounts for 30 to 40% of the nodules. The ^{235}U content of the nodules analysed ranges from 0 to 291 ppm.

Scope

The study of natural migration of uranium in porous unconsolidated sediments under brackish groundwater conditions may provide valuable information that can be used in the validation of models simulating radionuclide migration. These models are applied for the prediction of far-field migration as part of the safety assessment of geological disposal, e.g. in rock-salt. The brackish conditions are of relevance for this modelling of migration, because in aquifers directly overlying salt domes, salinity increases strongly with depth. Little is known about the influence of variable salt concentrations in groundwater on the processes of dissolution and migration of radionuclides.
At present, no natural-analogue studies relevant to radionuclide migration in unconsolidated sediments under brackish conditions are known. The great advantage of such a natural system is that it provides information about processes that have taken place on time and space scales required for repository safety assessments. Nevertheless, hydrogeochemical conditions and processes must be well characterized.

The uranium-enriched layer in the southwestern part of The Netherlands, occurs in an aquifer with brackish groundwater (Fig. 7). The paleohydrological localization of the area can be pin-pointed with great confidence. The present groundwater system is predominantly influenced by the proximity of the sea, and has therefore been subject to repeated alterations. The analogue will have particular relevance for the validation of models pertaining to long-term migration in areas considered for geological disposal in rock-salt formation as well as in other sites close to the sea.

Purpose

The analogue under study will provide information on the processes of dissolution and migration of uranium under varying natural geohydrochemical conditions. The analogue might also contribute to the understanding of the influence of variable salt concentrations in groundwater on the dissolution and migration processes. It might also add more confidence to our understanding of the processes determining migration under varying geohydrochemical and geohydrological conditions.

Finally, the natural analogue offers a base for the development of conceptual models for coupled geochemical and geohydrological processes. However, an understanding of the behaviour of radionuclide and other elements in waters with high ionic strength and the effect of high density on the groundwater flow system are vital preconditions for this coupling.

Field programme

For the old drillings, no groundwater samples are available. Because no screens were placed new samples cannot be taken. Furthermore, because no care was taken in the old boreholes to reduce chemical and mechanical disturbance to a minimum, the drilling samples in files are not useable for determination of geochemical parameters. For these reasons, a new borehole must be drilled, the first part of it with the use of traditional techniques up to a depth some metres distance from the upper nodule layer. After that, a newly developed technique will be used to reach the layer itself, in which great care will be taken to minimize chemical and mechanical disturbance. Both the groundwater and the rock material will be sampled and analysed to assess major and trace elements and the content of uranium, thorium, and radon. Some borehole measurements will be performed to obtain information about hydrogeological parameters, such as porosity and permeability, for formations of interest. Eh, pH, and probably some other geochemical parameters as well, will be measured down-hole.

Model validation aspects

The time-dependent geohydrochemical conditions will be reconstructed on the basis of available paleohydrological data for the area. With a geochemical code, which takes variations in ionic strength into account, and with a transport code, which considers variations in groundwater flow, the dispersion of dissolved species from the nodule layers into the aquifers will be calculated. The validation of the model will be performed by comparing the present-day and the predicted concentration profiles.

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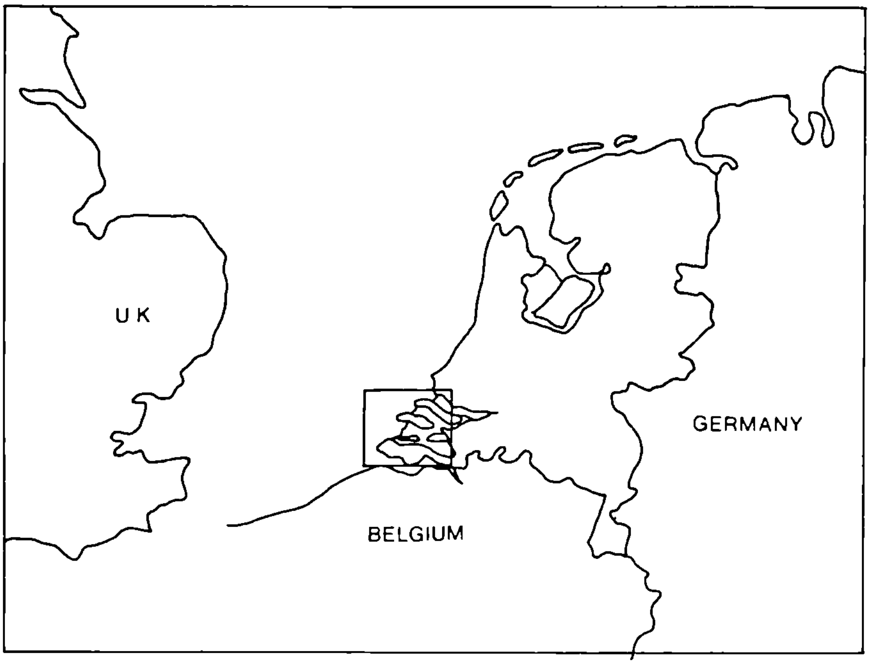

Figure 1 - Location of the study area in The Netherlands

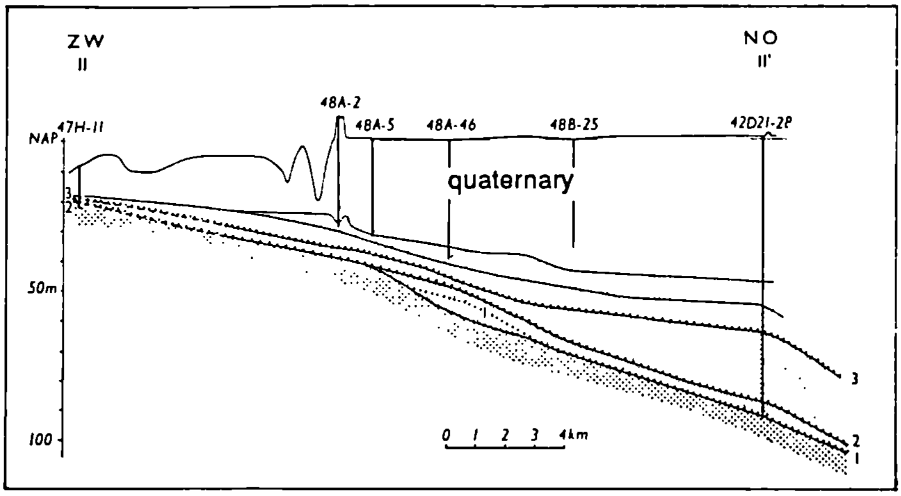

Figure 2 - Situation of the phosphorite nodule layers (After /3/)

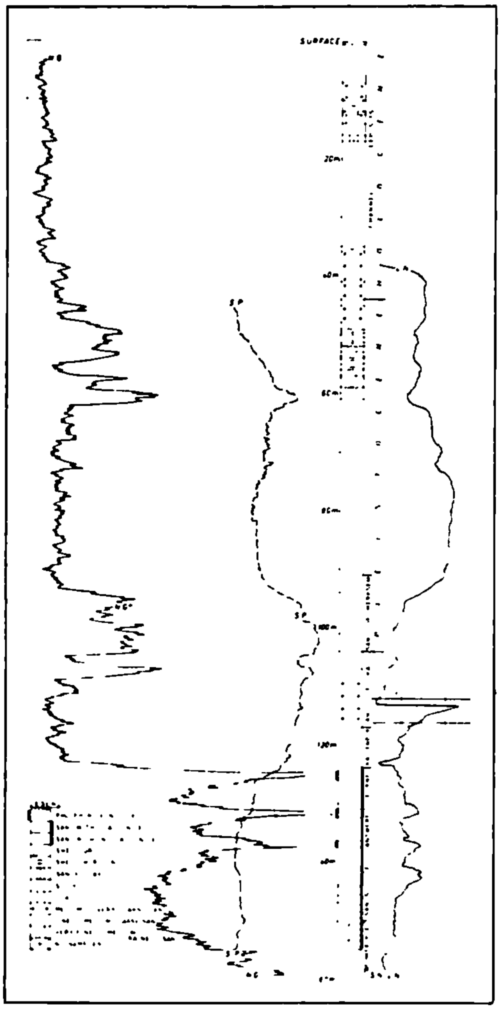

Figure 3 - Lithologic log of borehole 42B-20/3 with geophysical measurements (after /2/)

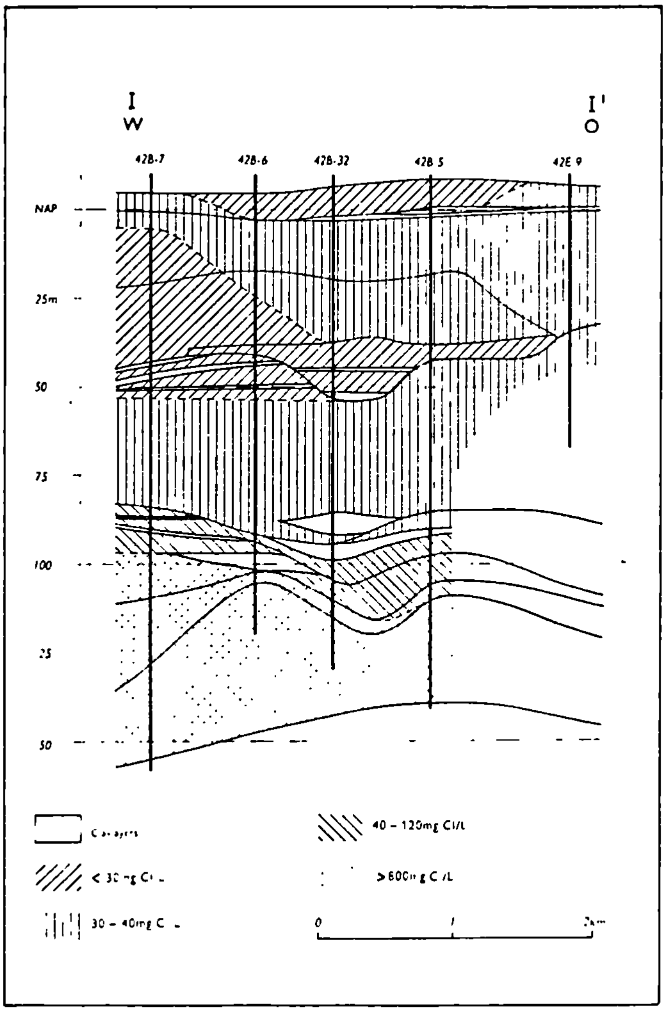

Figure 7 - Occurrence of clays and zones of equal chloride content in the section of dune area near Haamstede (after /1/)

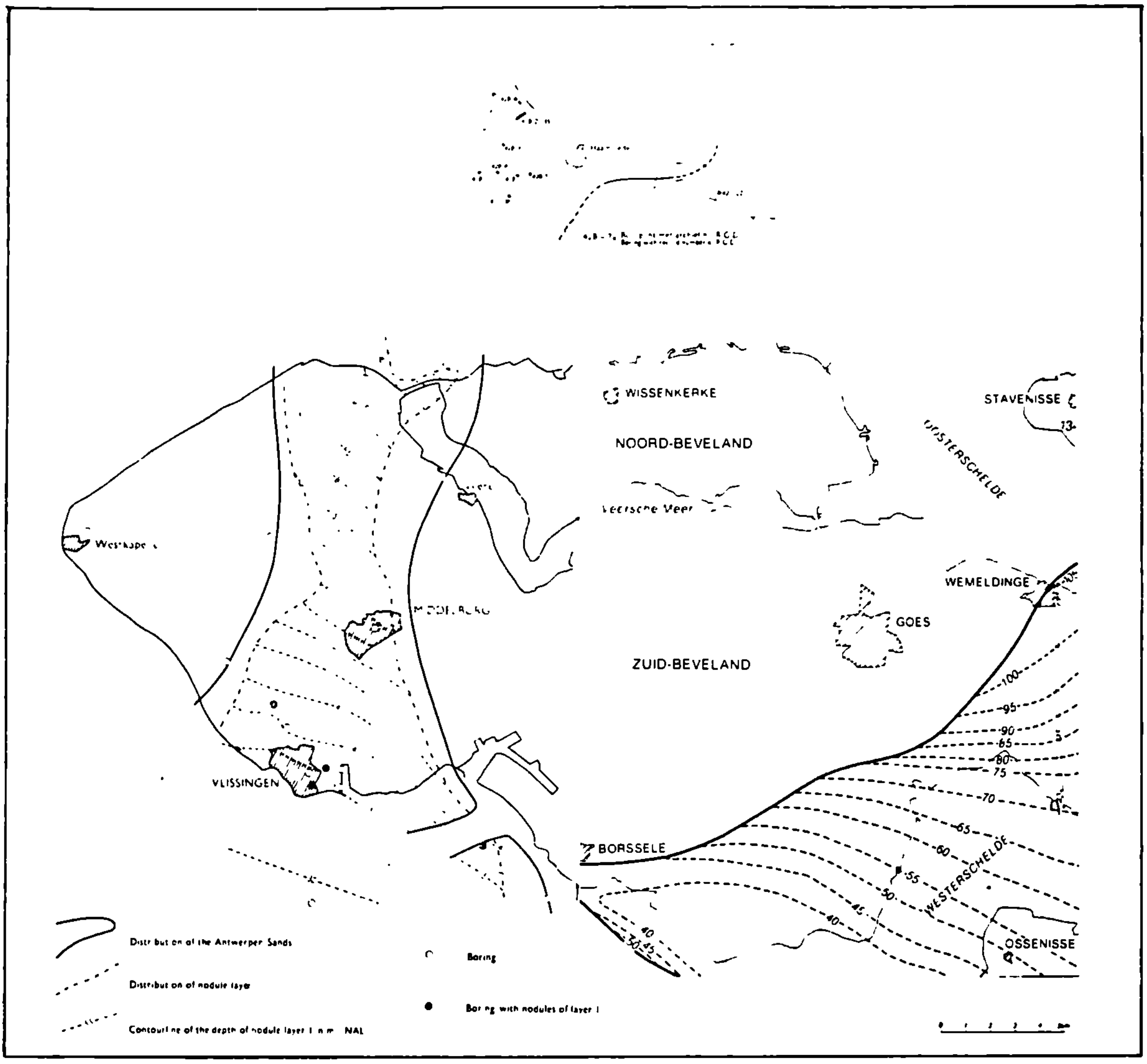

Figure 4 - Distribution and depth in m-MSL phosphorite nodule layer 1 (after /1/, /3/ and /4/)

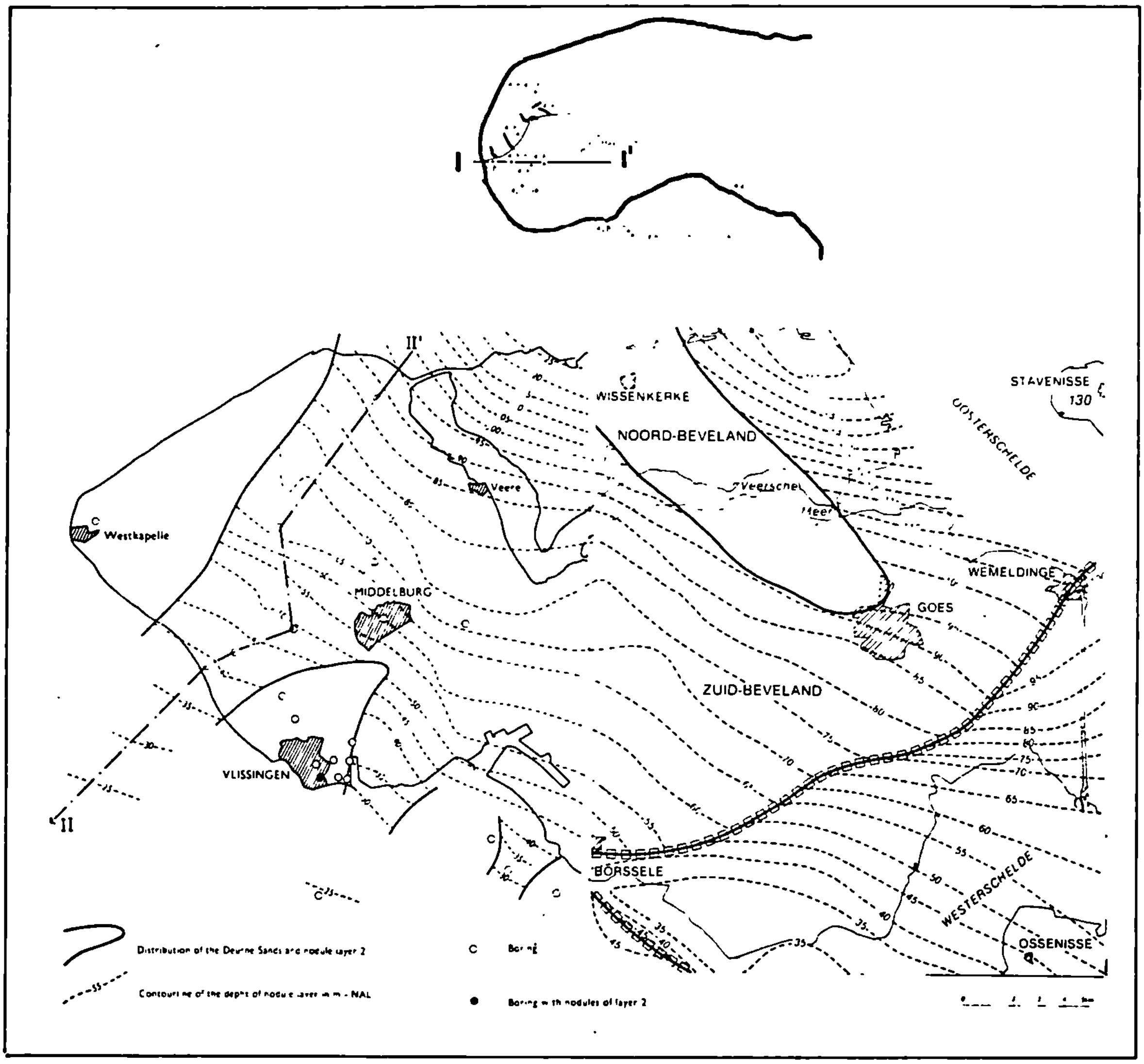

Figure 5 - Distribution and depth in m-MSL phosphorite nodule layer 2 (after /1/, /3/ and /4/)

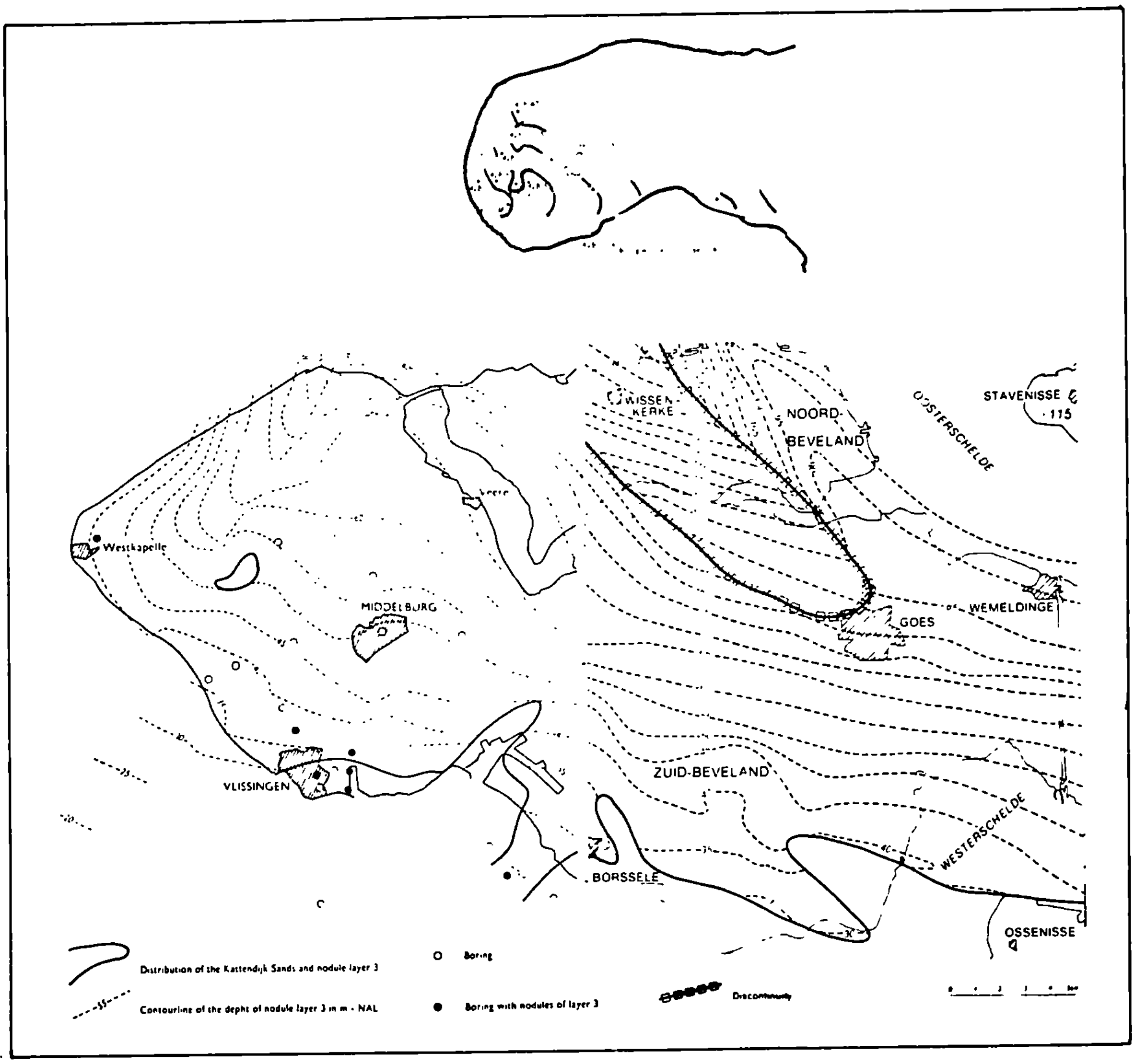

Figure 6 - Distribution and depth in m-MSL phosphorite nodule layer 3 (after /1/, /3/ and /4/)

Natural analogue studies in the radioactive waste research programme of Switzerland (status 1990 and bibliography)

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The study of natural analogues plays a significant rôle in the radwaste research programme of Switzerland. Natural analogues are used to identify potential problem areas for inclusion in the conceptual models of safety analysts and, more importantly, to verify and validate the various models or assumptions which are the component parts of a repository predictive safety assessment. To fulfil such requirements, a natural analogue study must be highly focussed and directed at specifically identified problems; it is always tempting, after all, to take a conventional study of a geochemical anomaly and add the tag "natural analogue" simply because some of the data may have some relevance to a particular aspect of radioactive waste management.

Switzerland has a relatively small nuclear waste disposal programme and, consequently, a conscious effort is put into every natural analogue project to ensure that it is relevant, focussed and addressing the points of immediate concern. Historically, there has always been a close interaction between those involved in planning natural analogue studies and the end users - predominantly safety assessment modellers, but also those involved in public relations. The major demonstration of the feasibility of nuclear waste disposal in Switzerland - Project Gewähr 1985 - thus contains sections on comparison with natural radioactivity and natural analogues (cf Project Gewähr, English summary, NGB 85-09, chapter 17). A widely distributed publicity brochure on natural analogues has also been printed by Nagra in 3 languages (German, French, Italian) and has recently been translated into Swedish by SKB.

The appended bibliography illustrates the wide range of studies which have been carried out in the last decade. In fact, this list only includes projects with major Swiss participation or funding which fall easily under the analogue label. This last aspect is particularly important as, for example, several literature reviews on materials longevity have been carried out which include significant analogue input while the extensive Nagra isotope hydrology programme contains many studies which could yield useful analogue data.

To date, Swiss natural analogue studies have covered many aspects of relevance to safety assessment studies and range across chemical speciation in groundwaters, colloid characterisation, uranium migration, matrix diffusion and redox processes. The projects range in size from one man studies to a cast of hundreds and in duration from two months to two years. Sites examined are also as varied: from a deep borehole in Böttstein, near Nagra's headquarters in north Switzerland, to a granite in southern Sweden and an alkaline spring in Oman.

Collaborators in the natural analogue programme have included SKB, Sweden, SURRC, BGS AEA Technology and Nirex, UK, AECL, Canada and, within Switzerland, Paul Scherrer Institute, University of Berne and, of course, Nagra's own staff.

Within the last couple of years, the analogue programme has been dominated by participation in the Poços de Caldos project with particular Swiss input in geological aspects (Uni Berne), colloids (PSI) and thermodynamic modelling (Uni Berne, PSI). Switzerland additionally hosted 3 very successful Poços modelling workshops held in Sarnen.

Increasingly, within the Swiss programme, emphasis is moving from HLW to L/ILW. This tendency is also reflected in the analogue programme with recent studies of pyrite oxidation in marl (a potential L/ILW repository host rock), the interaction between marl and concrete and radionuclide solubility in hyperalkaline waters. In this regard the recently initiated Jordan project, a collaborative venture with Ontario Hydro of Canada and UK Nirex is particularly important. As the study site in Jordan includes a natural deposit of "cement" minerals (e.g. Portlandite, Ettringite) which is rich in trace elements and lies within a bituminous marl, many processes relevant to L/ILW repository performance can be studied.

Finally, it may be noted that there is an increasing feeling within the Swiss nuclear community that efforts in public education need to be expanded. Emotive criticism of the nuclear waste management programme is particularly common, with the long timescales involved often being of concern. In this regard, we hope to considerably expand our use of natural analogues in public relations in the near future.

Presented below are all publications (to date) produced as part of Nagra's natural analogue programme, listed under rather loose subject headings for ease of reference. Further details may be obtained from the individual authors or from Nagra, Parkstr. 23, 5401 Baden, Switzerland.

1. Miscellaneous (overviews, relevance to safety analysis, general reports on the Swiss programme etc.)

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also published as
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and
KBS Technical Report 84-16, SKB Swedish Nuclear Fuel and Waste Management Co, Stockholm, Sweden.

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PREDICTIVE MODELLING OF THE GEOCHEMISTRY OF HYPERALKALINE GROUNDWATER IN THE MAQARIN AREA, JORDAN.

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Abstract

The current design concepts for low/intermediate level radioactive waste disposal in many countries involve emplacement in a cementitious repository situated in a host rock with a stable geology. This will provide a high pH chemical environment in the near-field, in which the solubility of radioelements is low and their sorption high. The investigation of natural analogues of the chemical environment around a repository forms an important part of repository safety research, as the behaviour of important radioelements can be inferred from studies of their solubility and speciation in systems which have evolved over geological timescales. Naturally occurring hyperalkaline groundwaters can be used as an analogue for cement pore water, and provides an ideal opportunity to carry out geochemical modelling of the speciation and solubilities of different trace elements under such LLW/ILW near-field conditions.

The following short report documents and compares the preliminary results of a 'blind' modelling exercise performed as part of a joint experimental and modelling programme focussed on the Maqarin area in Jordan. On the basis of the observed major element chemistry in a typical Jordan groundwater, participants in the modelling programme used geochemical models to predict the solubility/speciation of a number of trace elements (U, Th, Ra, Pb, Se, Sn and Ni). The predicitions were compared and the differences found could be readily traced to differences in the choice of thermodynamic data, rather than differences in the codes used. The predictions will be compared with the results of field work carried out in the Maqarin area in June 1990.

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Introduction.

The current design concepts for low/intermediate level radioactive waste disposal in many countries involve emplacement in a cementitious repository situated in a host rock with a stable geology. This will provide a high pH chemical environment in the near-field in which the solubility of radioelements is low and their sorption high. The safety case for such a repository design is supported by a large, integrated research programme of laboratory experiments, field measurements and modelling studies to predict the rate of release of nuclides and their subsequent transfer to the biosphere. The investigation of natural analogues of the chemical environment around the repository forms an important part of repository safety research as the behaviour of important radioelements can be inferred from study of their solubility and speciation in systems which have evolved over geological timescales. It thus provides data for interpretive modelling to improve our understanding of the physical and chemical processes that are likely to occur as the repository environment evolves with time, and potentially also a useful validation of both the models and the supporting thermodynamic data.

Natural hyperalkaline groundwater is found in some rather exotic geochemical environments and can be used as an analogue for cement pore water, and provides an ideal opportunity to carry out geochemical modelling of the speciation and solubilities of different trace elements under such L/ILW near-field conditions. A first study of this nature was carried out in Oman (Bath et al, 1987, McKinley et al 1988).

The current study is focussed on the Maqarin area of Jordan, which differs from other known occurrences of hyperalkaline discharge in that, like cement pore waters, the high pH values seem to be controlled by portlandite solubility rather than the alteration of ultramafic minerals. Values of pH above 12.0 are commonly found in groundwater seepages. The bed rock consists of limestones and marls, and hosts high concentrations of uranium and daughters, plus other trace elements associated with bituminous material, which should allow evaluation of the geochemical behaviour of a wide variety of elements at high pH and in the presence of some naturally occuring organic materials.

In the course of the Jordan natural analogue programme a number of geochemical phenomena associated with this hyperalkaline chemical environment are being investigated. These include:

i) solubility and speciation of major elements and trace elements

ii) the effect of organic complexation on the solubility of trace elements; and

iii) host rock alteration due to the ingress of these hyperalkaline waters.

The following short report documents and compares the preliminary results of "blind" modelling of the solution chemistry of a typical Jordan groundwater and represents the first stage of the modelling part of the project. Four groups of geochemical modellers are involved in the exercise: AEA Technology, Harwell (U.K.); Nationale Genossenschaft für die Lagerung radioaktiver Abfälle (Nagra), Baden (Switzerland), the Paul Scherrer Institute (PSI), Villigen (Switzerland), and the Ontario Hydro Research Division, Ontario (Canada).

Aims.

Geochemical speciation codes are used in the research work that underpins performance assessment to simulate the speciation and solubility of particular elements in solution. With some basic information as to chemical properties of the solution in question, such as pH, pE, and major element chemistry, it is possible to model the speciation of the elements of interest based on an assumption of thermodynamic equilibrium.

The aims of this preliminary "blind" modelling project are as follows:-

1. To test chemical models of elemental solubility/speciation under hyperalkaline conditions. On the basis of the observed major element chemistry, the geochemical models are used to predict the solubility/speciation of a number of trace elements (e.g. U, Th, Ra, Pb, Se, Sn and Ni).

2. To compare predictions from the participating groups in order to verify the different codes, (if the databases used in the modelling are identical), or to highlight differences between databases.

3. To compare the predicted chemistry with the observed chemistry, leading to a preliminary validation of the models.

The model solubility predictions are also useful to the analysts involved in the study as they provide a first estimate of expected concentration levels. In previous studies, discrepancies observed have shown up potential analytical problems. (Bath et al, 1987).

Methods.

The main speciation code used was PHREEQE (Parkhurst et al, 1980). This code, or an extended version of this code such as HARPHRQ at AEA Technology (Brown et al, 1990), was used by all four modelling groups. PSI for some of their modelling used the code MINEQL/PSI (Schweingruber, 1982). These codes simulate the speciation and solubility of particular elements in solution. The input information required for such simulations includes the basic chemical properties of the system in question, pH, pE, major element chemistry of the solution, and also a considerable amount of data on the thermodynamic relationships between the phases involved.

For the present modelling exercise, a typical groundwater analysis of this Jordan area was taken from Khoury et al (1985). This analysis is given in table 1. The temperature was assumed to be 25°C. The pH was measured at 12.5, and in the absence of measurements redox was varied with pE values of 0 (oxidising), -4 (intermediate), and -8 (reducing).

TABLE 1: GROUNDWATER COMPOSITION

Element	Concentration/M
Ca	1.2×10^{-2}
Na	2.93×10^{-3}
K	6.48×10^{-4}
CO_3	5.00×10^{-4}
Cl	2.15×10^{-3}
NO_3	5.00×10^{-5}
SO_4	2.83×10^{-3}

The trace elements studied were U, Th, Ra, Pb, Se, Ni, and Sn. It was suggested that for simplicity the concentrations of these elements be kept down to trace levels of 1.0×10^{-6}g/l. The resultant concentrations of each of the elements in question in moles is given in table 2.

TABLE 2: TRACE ELEMENT CHEMISTRY

Element	Concentration/M
U	4.2×10^{-9}
Th	4.3×10^{-9}
Ra	4.4×10^{-9}
Pb	4.8×10^{-9}
Se	7.0×10^{-9}
Ni	1.7×10^{-8}
Sn	8.4×10^{-9}

The above information is adequate to carry out computer simulations of the speciation of the trace elements concerned. In most simulations there was no attempt to equilibrate with solid phases, and only the solution chemistry and the degree of oversaturation or undersaturation of a range of potential solid phases modelled. PSI did, however, equilibrate with solids when carrying out the Pb, U and Th modelling.

It was noted that the given solution chemistry is not charge balanced, and has an excess negative charge. In order to maintain the pH, this charge imbalance was ignored during the simulations at AEA. At PSI, however, charge balance was obtained by reducing the OH^- concentration. Their justification for this was that, as hydroxide concentration can only be determined indirectly via the pH measurements this can yield uncertain results in strongly alkaline solutions. On equilibration only a very slight pH drop to 12.2 occurred and this was considered acceptable. In the following modelling it should be borne in mind, therefore, that there may be very slight discrepancies in the pH at which the modelling was performed by the various participating groups. This may affect reactions which are particularly pH dependent.

Preliminary Results.

The preliminary results are tabulated in tables 3 to 10. In general there was good agreement between the predictions of the various participating groups. Where discrepancies did occur they could all be readily traced to differences in the databases being used at the various participating organizations rather than to differences between the codes themselves. Thus the exercise has provided a useful code verification exercise.

Comparison between the results of the different modelling groups.

Nickel - The results of modelling at AEA, Nagra, and Ontario show close agreement (table 3) whereas PSI differs slightly. The main aqueous species is predicted by all four groups to be $Ni(OH)_3^-$. With the exception of PSI the controlling solid is thought to be $Ni(OH)_2$. The results of PSI differ due to the inclusion in their database of an extra aqueous species, $Ni(OH)_4^{2-}$, and an extra solid NiO (cf discussion in Baeyens and McKinley 1989). Baes and Mesmer (1976) indicate that at higher pH conditions such an aqueous species may be important, and in this respect the PSI predictions are probably more accurate. Predictions as to the identity of the solubility controlling phase are affected by uncertainty concerning the degree of crystallinity of the hydroxide and hence a large range of constants in the literature. The constant chosen dictates whether $Ni(OH)_2$ or NiO is the controlling phase. Silica is not defined for the Jordan water but may be an important constraint on Ni solubility. This is found for many groundwaters and also cement pore water (Baeyens and McKinley 1989). In cases which are reducing enough for sulphide to be present, extremely insoluble Ni sulphides may give rise to very low concentrations.

TABLE 3. NICKEL

Group	Aqueous species (%)		Controlling Solid	Saturation Index
Conditions: pH = 12.5, pE = 0				
AEA	$Ni(OH)_3^-$ $Ni(OH)_2^o$	97 3	$Ni(OH)_2$	-1.2
NAGRA	$Ni(OH)_3^-$ $Ni(OH)_2^o$	97 2	$Ni(OH)_2$	-1.2
PSI	$Ni(OH)_3^-$ $Ni(OH)_4^{2-}$	92 8	NiO	-2.8
ONTARIO	$Ni(OH)_3^-$ $Ni(OH)_2^o$	97 2	$Ni(OH)_2$	-1.2
There is no change from the above at pE values of -4 and -8.				

Lead - The results of AEA and Nagra modelling are identical (table 4) with the main aqueous species being $Pb(OH)_3^-$, and the controlling solid, $Pb(OH)_2$. PSI modelling, although predicting the same main aqueous species, shows that it may be necessary to consider another solid $Pb_3(CO_3)_2(OH)_2$ as well as $Pb(OH)_2$ when assessing lead solubility. Ontario modelling predicts the aqueous species, $Pb(OH)_4^{2-}$, to be dominant, and $Pb(OH)_2$ to be the controlling solid. The differences between the models can be attributed to differences in the lead databases used. The two lead databases used by AEA and Nagra were consistent. The database used by PSI appears to have differed with respect to some key aqueous species and solids. The Ontario database again gives different results, reflecting the use of a third Pb data set. The key species and solids concerned are $Pb(OH)_3^-$, $Pb(OH)_4^{2-}$, $Pb(OH)2$ and $Pb_3(CO_3)_2(OH)_2$.

The predicted high solubility of Pb under hyperalkaline conditions has been verified in experimental studies of cement pore waters (Bayliss et al, 1987)

TABLE 4. LEAD

Group	**Aqueous species (%)**		**Controlling Solid**	**Saturation Index**
Conditions: pH = 12.5, pE = 0				
AEA	$Pb(OH)_3^-$	100	$Pb(OH)_2$	-5.5
NAGRA	$Pb(OH)_3^-$	100	$Pb(OH)_2$	-5.5
PSI	$Pb(OH)_3^-$ $Pb(OH)_2^o$	94 6	$Pb_3(CO_3)_2(OH)_2$ and/or $Pb(OH)_2$	undersaturated
ONTARIO	$Pb(OH)_4^{2-}$ $Pb(OH)_3^-$	93 7	$Pb(OH)_2$	-2.12
AEA, NAGRA and Ontario predicted no change from the above at pE values of -4 and -8. PSI predicted no change at pE = -4, but did predict a change at pE = -8:-				
PSI	$Pb(OH)_3^-$ $Pb(OH)_2^o$	94 6	PbS_2	undersaturated

Radium - Only AEA Technology and Nagra carried out modelling on radium speciation and obtained the same results i.e. Ra^{2+} as the main aqueous species, and $RaSO_4$ as the controlling solid (table 5). It should be noted however that these databases were limited (Ra^{2+}, $RaOH^+$ and $RaSO_4^0$ only as aqueous species, and the solids $RaCO_3$ and $RaSO_4$). More data on radium chemistry are available and some additional simulations were carried out at AEA with additional data from Benson and Teague (1980), Langmuir and Riese (1985). These data included a modified constant for $RaSO_4$, extra aqueous species, $RaCO_3^0$ and $RaCl^+$, additional solids, pure Ra and $RaCl_2.2H_2O$, as well as modified constants for the already present solids. These simulations showed different speciation, predicting 75% Ra^{2+}, 20% $RaSO_4$ and 4% $RaOH^+$. The identity of the solubility controlling phase remained the same. The presence of only one reaction concerning the hydrolysis of radium is reasonable due to the fact that as one moves down the periodic table in this group the elements show less and less tendency to hydrolyse (Baes and Mesmer, 1976).

TABLE 5a. RADIUM				
Group	**Aqueous species (%)**		**Controlling Solid**	**Saturation Index**
Conditions: pH = 12.5, pE = 0				
AEA	Ra^{2+} $RaOH^+$	96 4	$RaSO_4$	-1.3
NAGRA	Ra^{2+} $RaOH^+$	96 4	$RaSO_4$	-1.3
PSI	-	-	-	-
ONTARIO	-	-	-	-
There is no change from the above at pE values of -4 and -8.				
Some additional simulations were carried out by AEA with a modified and extended radium database (Benson and Teague, 1980; Langmuir and Reise, 1985):-				
Conditions: pH = 12.5, pE = 0				
AEA	Ra^{2+} $RaSO_4^o$ $RaOH^+$	75 20 4	$RaSO_4$	-1.6
There is no change from the above at pE values of -4 and -8.				

Thorium - Thorium speciation was modelled by AEA, Nagra and PSI. In all three cases $Th(OH)_4^o$ was found to be the main aqueous species, and ThO_2 the solubility controlling phase (table 6). In all three models the solid phase was oversaturated. The inclusion of a more crystalline ThO_2 solid in the Harwell database explains the smaller predicted solubility of thorium in this case (cf discussion of effects of ThO_2 crystallinity by Langmuir and Hermann (1980)).

TABLE 6. THORIUM				
Group	**Aqueous species (%)**		**Controlling Solid**	**Saturation Index**
Conditions: pH = 12.5, pE = 0				
AEA	$Th(OH)_4$	100	ThO_2	+5.7
NAGRA	$Th(OH)_4$	100	ThO_2	+1.2
PSI	$Th(OH)_4$	100	ThO_2	oversaturated
There is no change from the above at pE values of -4 and -8.				

Selenium - AEA, PSI and Nagra show very close agreement in the predicted speciation with SeO_3^{2-} as the dominant aqueous species and $CaSeO_3$ as the controlling solid (table 7). Ontario, however, predicts different species, and a different controlling solid. Ontario has used a different database which, furthermore, does not include the solid phase $CaSeO_3$. Elemental Se is known to form in particular reducing environments (eg roll front deposits) but this is usually associated with microbial sulphate reduction (Granger and Warren, 1969). Solubility control by elemental Se has also been predicted for a range of reducing groundwaters (Baeyens and McKinley 1989).

TABLE 7. SELENIUM

Group	Aqueous species (%)		Controlling Solid	Saturation Index
Conditions: pH = 12.5, pE = 0				
AEA	SeO_3^{2-}	100	$CaSeO_3$	-5.3
NAGRA	SeO_3^{2-}	100	$CaSeO_3$	-5.4
PSI	SeO_3^{2-}	100	$CaSeO_3.H_2O$	-5.3
ONTARIO	Se_2^{2-} SeO_3^{2-}	45 10	Se	145.3
Conditions: pH = 12.5, pE = -4 *AEA and PSI show no change from above.*				
NAGRA	SeO_3^{2-}	100	Se	-7.7
ONTARIO	Se_2^{2-}	50	Se	137.3
Conditions: pH = 12.5, pE = -8				
AEA	HSe^- Se^{2-}	99 1	Se	-3.9
NAGRA	HSe^- Se^{2-}	99 1	Se	-4.0
PSI	HSe^- Se^{2-}	99 1	Se	-4.0
ONTARIO	Se_2^{2-}	50	Se	129.3

Tin - Tin modelling was carried out by AEA and Nagra. AEA predict the aqueous species to be dominated by $Sn(OH)_6^{2-}$, whereas Nagra predict $Sn(OH)_3^-$ to be dominant (table 8). In both simulations the controlling solid was predicted to be SnO_2, but the solubilities were different. AEA predict a considerably higher solubility with undersaturation of the solid phase, whereas Nagra predict a low solubility and oversaturation. The difference in the results is due to the inclusion in the AEA database of data for tin(IV) hydrolysis products. At high pH conditions these have been shown to be important at temperatures above 100°C (Kuril'chikova and Barsukov, 1970). The solubility of SnO_2 (cassiterite) has been shown to increase at high pH associated with the appearance of the tin(IV) species $Sn(OH)_5^-$ (Barsukov and Klintsova, 1970). These additional experimental data support the inclusion of these extra data in the database. The AEA predictions therefore probably approach the realistic situation more closely in this instance.

TABLE 8. TIN

Group	**Aqueous species (%)**		**Controlling Solid**	**Saturation Index**
Conditions: pH = 12.5, pE = 0				
AEA	$Sn(OH)_6^{2-}$	84	SnO_2	-3.8
	$Sn(OH)_5^-$	15		
NAGRA	$Sn(OH)_3^-$	100	SnO_2	24.6
PSI	-	-	-	-
ONTARIO	-	-	-	-
Conditions: pH = 12.5, pE = -4 *AEA showed no change from above*				
NAGRA	$Sn(OH)_3^-$	100	SnO_2	16.6
Conditions: pH = 12.5, pE = -8 *AEA showed no change from above*				
NAGRA	$Sn(OH)_3^-$	100	SnO_2	8.6

Uranium - For this element there is little consensus between the four participating groups in both aqueous speciation and controlling solid phase (table 9). This situation was also evident in the previous Oman study (Bath et al, 1987). Differences are due to differences in the data selected for use in the models. A major difference also between the models is the choice of solid. There is some debate as to whether uranium hydroxide solids or the calcium or sodium uranates will control solubility under high pH conditions. A recent report by Lemire (1988) would indicate that at a pH of 12.5 it is likely that calcium uranate is the stable solid phase except under particularly reducing conditions when UO_2 is the stable phase.

As a general comment, it was noted that in all of the solutions modelled, the solution was oversaturated with respect to calcite. In order to assess the effect equilibration with calcite might have on the predictions, some simulations were carried out by AEA which equilibrated with this phase. It was found that there was no change to the predicted chemistry at all, except under reducing conditions when very slight changes in the aqueous speciation were noted.

TABLE 9. URANIUM

Group	**Aqueous species (%)**		**Controlling Solid**	**Saturation Index**
Conditions: pH = 12.5, pE = 0				
AEA	$UO_2(OH)_4^{2-}$ $UO_2(OH)_2^{o}$	87 13	$CaUO_4$	10.2
NAGRA	$UO_2(OH)_3^-$	100	$UO_3.2H_2O$	-5.6
PSI	$UO_2(OH)_3^-$	100	$Ca_2UO_2(OH)_4$	oversaturated
ONTARIO	$UO_2(CO_3)_3^{4-}$ $(UO_2)_3(OH)_5^+$ $UO_2(CO_3)_2^{2-}$ $U(OH)_5^-$	60 11 4 2	U_3O_8	0.23

TABLE 9 contd. URANIUM

Conditions: pH = 12.5, pE = -4				
AEA	$UO_2(OH)_4^{2-}$	85	$CaUO_4$	10.2
	$UO_2(OH)_2^{o}$	13		
	$UO_2(OH)_2^{-}$	2		
NAGRA	$UO_2(OH)_3^{-}$	100	UO_2	-3.2
PSI	$UO_2(OH)_3^{-}$	100	$Ca_2UO_2(OH)_4$	oversaturated
ONTARIO	$U(OH)_5^{-}$	>99	UO_2	-3.1
Conditions: pH = 12.5, pE = -8				
AEA	$U(OH)_4^{o}$	91	U_4O_9	7.9
	$U(OH)_5^{-}$	7		
	$UO_2(OH)_2^{-}$	2		
NAGRA	$UO_2(OH)_3^{-}$	64	UO_2	4.6
	$UO_2(OH)_2^{-}$	32		
	$UO_2(CO_3)_3^{5-}$	2		
PSI	$UO(OH)_5^{-}$	100	$Ca_2UO_2(OH)_4$	oversaturated
ONTARIO	$U(OH)_5^{-}$	>99	UO_2	-3.1

Some additional simulations were carried out at Ontario (Dayal and Eagleson 1990) using higher initial concentrations of the trace elements (at $1.0x10^{-3}$ g/l rather than $1.0x10^{-6}$g/l) to determine the sensitivity of the results to trace element concentrations. These results are shown in table 10. In the case of nickel and lead, it can be seen that the aqueous speciation has not changed, nor has the identity of the controlling solid. The higher concentrations, however, have led to the oversaturation of the solid phase in solution. However, for uranium both the aqueous speciation and the identity of the controlling solid have changed.

TABLE 10. THE EFFECT OF HIGHER TRACE ELEMENT CONCENTRATIONS
(Simulations carried out at Ontario)

Aqueous species (%)		Controlling Solid	Saturation Index
Conditions: pH = 12.5, pE = 0			
NICKEL			
$Ni(OH)_3^-$ $Ni(OH)_2^o$	97 3	$Ni(OH)_2$ Bunsenite	1.84 0.19
LEAD			
$Pb(OH)_4^{2-}$ $Pb(OH)_3^-$	97 3	$Pb(OH)_2$	0.88
URANIUM			
$(UO_2)_3(OH)_5$	33	Schoepite	1.98

Conclusions.

An important conclusion from the above comparisons is that the differences in predictions from different modelling groups can be attributed to differences in the choice of data for use in the models rather than differences in the codes themselves. Often these are due to a lack of experimental data from which to deduce the necessary constants.

An important point to be borne in mind also, is that close agreement between the four different modelling groups with respect to chemical predictions does not necessarily indicate that the predictions are correct. The use of chemical speciation codes is very reliant on the quality of the data available on which to base the calculations and it must be remembered at all times that reliable data are essential for the use of these models. The correct identification of the solubility controlling solid phase and/or accurate representation of solid solution effects will also be important in future solubility modelling.

The next stage of this work concerns comparison of the predicted chemistries with the observed results. This awaits the results of field work carried out in the Maqarin area.

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POSSIBLE ANALOG RESEARCH SITES FOR THE PROPOSED HIGH-LEVEL NUCLEAR WASTE REPOSITORY IN HYDROLOGICALLY UNSATURATED TUFF AT YUCCA MOUNTAIN, NEVADA

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Summary

The distinctive characteristics of the candidate high-level nuclear waste repository at Yucca Mountain, Nevada must be considered in the application of analog studies to the evaluation of its performance. The proposed site is in a fractured, welded, devitrified, silicic ash flow tuff in a sequence of silicic tuffs. The repository horizon would lie above the groundwater table in a chemically oxidizing environment. The Peña Blanca deposits in the Chihuahua City uranium district, Mexico, and the Akrotiri Peninsula archaeological site on Santorini, Greece can be regarded as analogs of the proposed high-level nuclear waste repository system at Yucca Mountain, Nevada. Both occur in hydrologically unsaturated, silicic tuffaceous rocks in arid to semi-arid environments comparable to Yucca Mountain. Studies of these systems could permit identification and characterization of processes that would occur as radionuclides are released from the candidate repository to the geologic environment, and could aid in the development and validation of predictive models for the evolution of the Yucca Mountain repository system.

Introduction

In 1987 the Congress and President of the United States of America specified Yucca Mountain, Nevada as the national candidate site for geologic disposal of high level nuclear waste (HLW) . At present, the site is undergoing characterization by the US Department of Energy (DOE) to determine whether or not it is suitable for a repository. The US Nuclear Regulatory Commission also conducts research relevant to the Yucca Mountain site to support the repository licensing process. The Yucca Mountain site differs from those currently under investigation in other countries for permanent disposal of HLW in that the proposed repository horizon is in the hydrologically unsaturated, chemically oxidizing zone of a volcanic tuff. Sites under consideration elsewhere occur in a variety of host rocks, but they are generally in hydrologically saturated rocks in chemically reducing environments (IGC, 1989).

A variety of analogs of the proposed Yucca Mountain repository system have been considered including the warm and hot springs of the Yellowstone geyser system in Wyoming (e.g. DOE, 1988) and interflow thermal effects at the Valles Caldera, New Mexico (Krumhansl and Stockman, 1988). Alexander and Van Luik (1990) summarize DOE natural analog studies for the Yucca Mountain site, and propose research on radionuclide transport at the uranium deposits in the McDermitt Caldera on the Nevada-Oregon border. Another intriguing set of analogs is the environments of underground explosions of test nuclear devices on the Nevada Test Site (NTS). Some of these tests have been in the hydrologically unsaturated zone of lithologically similar rocks. Studies of the transport of radionuclides from other test sites at the NTS have revealed important results such as the negligible retardation of Ru-106 (Coles and Ramspott, 1981) and I-129 migration rates which exceed that of tritium (Thompson, 1985).

Because they share many features essential to nuclear waste migration phenomena, the geologic settings of the Peña Blanca deposits in the Chihuahua City uranium province, Mexico, and the Akrotiri Peninsula archaeological site on Santorini, Greece can be regarded as analogs of the Yucca Mountain repository system. Research at these sites could permit identification and characterization of processes that would occur as radionuclides are released from the candidate repository to the geologic environment, and could aid in the development and validation of predictive models for the evolution of the Yucca Mountain repository which are essential for licensing. The object of this paper is to illustrate similarities between Yucca Mountain, Peña Blanca, and Santorini, with particular reference to processes of alteration and transport of analogs of radioactive contaminants in the geologic environment.

Yucca Mountain, Nevada

Yucca Mountain is 150 km northwest of Las Vegas, Nevada on federal land including part of the NTS. Geologic information about the Yucca Mountain area has been gathered since the early 1900's. Work was initially directed toward mineral and energy resource exploration; more recently, studies have been connected with government activities at the NTS. Since 1977, the DOE has gathered considerable information on Yucca Mountain, and the information presented below is drawn largely from that collection (e.g. DOE, 1988).

Yucca Mountain lies in a hydrologically closed basin in the southern part of the Great Basin physiographic province, which is bounded to the east by the Colorado Plateau and to the west by the Sierra Nevada Range. The Great Basin is a product of continental extension over the last 20 Ma and is characterized by north-south trending horsts and grabens which are offset by widely spaced regional strike slip faults. The southern part of the basin is composed of heavily eroded tilted-block ranges and sediment filled valleys. Tectonic features near Yucca Mountain are dominated by normal faults and other extensional structures. Yucca Mountain consists of a series of north-trending structural blocks which have been tilted eastward by west-dipping, high-angle normal faults related to Basin and Range tectonism over the last 7 Ma.

At Yucca Mountain a series of silicic volcanic units with a thickness ranging from 1 to 3 km rests on Silurian dolomite. These volcanic rocks are variably welded, devitrified and altered ash flow and air fall tuffs with minor volcanic flows and breccias. The oldest of the silicic volcanic units at Yucca Mountain was deposited about 14 Ma ago and the youngest is about 12 Ma old. Subsequent small scale basaltic volcanism has occurred near Yucca Mountain episodically into the Pleistocene Epoch.

The proposed repository horizon is in a devitrified rhyolite ash-flow tuff unit in the Topopah Spring Member of the Paintbrush Tuff, which was deposited 12 - 13 Ma ago and is about 300 m thick at Yucca Mountain. The basal welded vitrophyre of the Topopah Spring Member grades upward into a densely welded, devitrified, nonlithophysal zone from 27 to 56 m thick which is the proposed location of the repository. This zone is phenocryst poor (2 - 22%); the phenocrysts include sanidine, plagioclase (andesine to oligoclase), and minor quartz, biotite, amphibole, iron-titanium oxides, allanite, and zircon. The primary groundmass of the Topopah Spring Member is glass and/or devitrification products comprising alkali feldspar and silica minerals. Smectite and the silica-rich zeolite minerals clinoptilolite and mordenite are dominant alteration products. In some areas primary glass is completely converted to zeolites. Overall, the Topopah Spring Member averages about 70-80% SiO_2 (Byers, 1985). Approximately 10 m beneath the Topopah Spring Member is a layer 30 - 300 m thick which is locally rich in zeolites (60 - 80 % clinoptilolite and mordenite).

The saturated zone groundwaters from tuffaceous aquifers at Yucca Mountain are dilute ($<10^{-2}$ m), oxidizing, sodium bicarbonate solutions, rich in silica, with lesser calcium, potassium, magnesium, chloride, sulfate, nitrate, and fluoride. Information about the pore waters in the unsaturated zone is limited at this time. The proposed repository horizon is about 200 m above the water table in rocks with porosity that is thought to be 40 to 70% saturated with water. In this low pressure medium, water would vaporize as the temperature increases in the near field. Water movement in the unsaturated zone is thought to be slow (e.g. 0.5 mm/yr) if it is dominated by matrix flow. The chemistry, distribution and behavior of water in unsaturated, fractured tuffs is incompletely understood particularly under conditions of thermal perturbations, and is currently a subject of investigation.

Yucca Mountain is in a mid-latitude desert climate with average annual precipitation less than 15 cm and average temperature of about 13°C. Only about 0.3% of the local precipitation is thought to penetrate to the deeper portions of the unsaturated zone. A variety of evidence (e.g. pack rat middens and palynology) suggests that the climate has been arid to semi arid for the last 2 Ma. The aridity of the region results in little groundwater recharge and hence a low rate of groundwater movement. The groundwater in southern Nevada does not discharge into rivers or large bodies of surface water; rather, it discharges by evapotranspiration (e.g. at Alkali Flats, California) and at springs (e.g. at Death Valley, California).

Peña Blanca, Mexico

The Peña Blanca district is in northern Mexico about 50 km north of Chihuahua City and is part of the Chihuahua City uranium province. Many of the uranium deposits in the district have been drilled and/or developed by underground or open pit mining over a period of 20 years (Goodell, 1981); however, there is presently no mining activity at Peña Blanca. Combined, these deposits include more than 2000 metric tons of U_3O_8 and constitute the bulk of Mexican uranium resources.

Peña Blanca is part of the northern Mexico basin and range system and lies near the boundary between a stable craton to the west and a more mobile belt to the east (Goodell, 1985). The regional structural province is bounded to the east by the Trans-Pecos Range and to the west by the Sierra Madre Occidental (George-Aniel et al., 1985). The Sierra Peña Blanca is a west dipping horst block with a superimposed set of parallel northwest-striking normal (extensional) faults.

Peña Blanca stratigraphy consists of a sequence of mid-Cretaceous (Albian to Cenomanian) limestones and mudstones on which a series of Tertiary silicic volcanics has been deposited (Cardenas-Flores, 1985). Host rocks for the uranium deposits are the Escuadra and Nopal Formations comprising outflow facies of variably welded tuffs with air-fall, ignimbrite, vitrophyre, lahar, and water-worked units. The preserved total thickness of the volcanic units varies over the Sierra Peña Blanca area from 106 to 538 m, and rock ages range from 44 Ma to 35 Ma (Goodell, 1981).

The Peña Blanca tuffs are generally devitrified rhyolitic ignimbrites consisting largely of glass devitrified to cristobalite and feldspar with quartz, sanidine and minor biotite phenocrysts (Cardenas-Flores, 1985). These tuffs have SiO_2 contents between 63 and 78%, Al_2O_3 at 11 to 14%, and K_2O at 4 to 7% (Goodell, 1981). Background uranium concentrations of the tuffs range from about 4 to 10 ppm (George-Aniel et al., 1985). Uranium in the ores was likely derived from the alteration of volcanic glass in the tuffs by convective hydrothermal groundwater systems. Uranium deposits, tentatively dated at 3.5 Ma, are commonly associated with minor hydrothermal alteration at faults, fractures, and breccias and are underlain by an extensive, unwelded, zeolitized tuff (part of the Nopal Formation). Fluid inclusion evidence suggests mineralization by low salinity (0 - 4.94 wt % NaCl equiv.), moderate temperature (150 - 250°C) fluids (George-Aniel et al., 1985). The present uranium mineralization is predominantly uranyl silicates and vanadates (Goodell, 1981); however, the sparse occurrence of uraninite and other reduced phases (e.g. pyrite) indicates that original uranium (IV) mineralization has been oxidized. Some areas of Peña Blanca mineralization contain enough cesium to form magaritasite (Cs carnotite) $(Cs,K,H_3O)_2(UO_2)_2V_2O_8{\bullet}H_2O$ (Wenrich et al., 1982) in addition to the uranium minerals.

The distribution of uranium indicates that mineralizing hydrothermal fluids circulated primarily in faults and fractures, although there is dispersed uranium mineralization in areas with low fracture permeability (Goodell, 1981), suggesting that matrix flow was important locally. Stratigraphic control appears to have been important to ore localization in all deposits, with characteristics such as secondary porosity, brecciated zones, and fissures controlling detailed ore distribution (Cardenas-Flores, 1985). There is general agreement that the ores were emplaced by a geothermal, convecting groundwater system (Goodell, 1981; Goodell, 1985; Cardenas-Flores, 1985) which may have had significant inputs of volcanic fluids (George-Aniel et al., 1985) in addition to dominant meteoric waters (Goodell, 1985).

All of the Peña Blanca uranium deposits are presently above the water table in the unsaturated zone. At present, uranium is being remobilized by oxidizing meteoric groundwaters which episodically penetrate the deposits through fractures in the unsaturated tuffs. The climate in the Peña Blanca area is arid, with annual precipitation of about 24 cm and average annual temperature of 19° C.

Similarities between the geologic settings of the proposed high level waste repository site at Yucca Mountain and the uranium deposits at Peña Blanca suggest that a variety of present and past processes at Peña Blanca are analogous to those that could affect radionuclide migration at Yucca Mountain. The oxidation of Peña Blanca uraninite, the resulting dispersion of uranium from the sites of original mineralization, and the formation of secondary uranyl silicates are analogous to processes that may affect spent nuclear fuel and elemental migration at the repository. The behavior of Cs in some of the ores may be analogous to that of Cs from HLW. Processes in the zeolitized horizon underlying the ore deposits at Peña Blanca may also constitute good analogs of radionuclide retardation in zeolitized tuffs at Yucca Mountain.

Information required for a thorough study of the Peña Blanca analog site includes primary and alteration mineralogies of the ores and host rocks. The spatial distributions of these minerals and their temporal relations must be ascertained. Knowledge of the chemical compositions of the ores and host rocks with regard to both major and trace elements, and especially the compositions of individual mineral phases within the ores and the distributions of important radionuclides and analog elements within the minerals are required. Determination of the hydrological relations in the area of the deposit both at the present and in the past are necessary. Groundwater compositions must be measured, including spatial variations.

The factors listed above are all measurable; however, as with many natural analogs, it may be difficult to place limits on the initial and boundary conditions for alteration and transport processes at Peña Blanca. The timing of the onset of oxidation of the ores is important to elemental migration studies and may remain uncertain. The original distribution of the uraninite and other ore constituents can only be inferred from the present distribution. Changes and durations of changes in the hydrology in the past may remain unknown. It is likely that the hydrothermal systems responsible for forming the ores have complex histories; it may be difficult to separate the variable hydrothermal alteration and remobilization of the ores from the effects of later meteoric fluids.

Santorini, Greece

The eruption at Stronghyle volcano in approximately 1645 B.C. (Hammer et al., 1987) buried a Minoan city under volcanic debris on what is now the Akrotiri peninsula on the island of Thera, Santorini. This event was one of the largest explosive eruptions in post-glacial time; a caldera with an area of 83 km^2 and a depth of 600-800 m was formed (Watkins et al., 1978). Since archaeological excavations began in 1967, much information has been unearthed regarding the archaeology and geology of the area. Investigations at the site are ongoing.

Santorini comprises a complex of volcanos located about 100 km north of Crete. Prior to the 1645 B.C. eruption, the single large island of Stronghyle occupied the area of the Santorini group. The great eruption destroyed Stronghyle and left the islands of Thera, Therasia, and Aspronisi as remnants. During the past 1800 years, the islands of Palea and Nea Kameni have formed in the caldera by submarine and subaerial volcanism (Pichler and Kussmaul, 1980). All of the eruptions have been confined to a 3-4 km wide, northeast trending graben which formed as a result of extension in the eastern Mediterranean over the past 10 Ma (Heiken and McCoy, 1984).

The oldest subaerial volcanic activity at Santorini deposited ash and pumice on Lower Tertiary phyllite basement approximately 1 Ma ago. Volcanic activity continued intermittently, depositing 30 to 90 m of pumice, ash, and lava flows on the island. The Minoan eruption buried settlements under 30 m of volcanic sediment (Pichler and Friedrich, 1980). Four phases of this eruption have been identified (Heiken and McCoy, 1984): 1) plinian eruption with massive pumice fall; 2) phreatomagmatic base surge of fine ash and pumice lapilli; 3) phreatomagmatic eruption of pumice bombs, lithic fragments, ash, and including distal mudflows; and 4) ignimbritic eruption deposited at temperatures greater than 500°C (Wright, 1978). All of the Minoan eruption phases deposited pyroclasts of rhyodacitic composition (Heiken and McCoy, 1984). Paleosols are preserved in several places below the Minoan tuff and locally reach thicknesses of 3-4 m. These paleosols developed on the series of welded tuffs and ignimbrites upon which the buildings of Akrotiri (the largest of the known Minoan towns buried by the eruptions) were founded (Pichler and Friedrich, 1976).

The anthropological horizon at Akrotiri is located in the unsaturated zone above the groundwater table. In the semi-arid climate the mean annual precipitation is essentially equivalent to the estimated annual evapotranspiration loss (approximately 35 cm/year, mean air temperature is 17° C) (Marinos and Marinos, 1978). The hygroscopic character of the upper soil layers generally prevents deep infiltration of rain water even though the deeper soils appear to be permeable (Marinos and Marinos, 1978). In the Akrotiri area, steep-sided gullies have been cut into the tephra sequence by runoff after exceptionally heavy rains. Paleoclimatological data indicate that the climate on Santorini at the time of its eruption did not differ strongly from the present climate; air temperatures were slightly warmer and the climate was slightly more arid (McCoy, 1980).

Elemental migration at the Akrotiri site, analogous to that which would occur at the Yucca Mountain repository, could possibly be well constrained chemically, temporally, and spatially using artifacts as analogs for contaminant sources. For example, numerous lead balance weights discovered at this site have distinct chemical compositions (Gale and Stos-Gale, 1981). Oxidation rinds developed on the lead weights (Petruso, 1978) suggest that some components have been released during alteration. Artifacts may therefore constitute well constrained point sources for dispersion of trace species analogous to migration of waste elements at Yucca Mountain. The known period of 3600 years between the eruption of Santorini and the present corresponds well to the time frame of interest in the evaluation of the HLW repositories. The rock types enclosing the archaeological site are similar to those at Yucca Mountain, and the climates and hydrological relations are comparable.

Information required for a detailed study of the Santorini analog site includes compositions of lead weights or other artifacts (major and trace elements). Mineralogy and composition of the alteration products of the artifacts (e.g. oxide coatings), and knowledge of the primary and alteration mineralogy of the rocks surrounding the artifacts is required. Bulk chemical compositions of the rocks surrounding the weights must be measured as a function of location, with particular emphasis on concentration gradients of (trace) elements derived from the artifacts. Present and former hydrological relations in the area of the contaminant analogs and groundwater compositions (including local variations) are also of importance.

Conclusions

Uranium deposits at Peña Blanca, Mexico and archaeological sites at Santorini, Greece offer good analogs of processes that would be expected to occur in the geologic setting of the proposed HLW repository at Yucca Mountain, Nevada. The sites at both Peña Blanca and Santorini are in the hydrologically unsaturated zone of siliceous tuff sequences, and both sites occur in climates similar to that of southern Nevada. The past and present oxidation of uraninite at Peña Blanca constitutes an analog for the alteration of spent nuclear fuel. The processes of migration of uranium and other elements from sites of initial mineralization under unsaturated, oxidizing conditions at Peña Blanca are analogous to those that would occur in the Yucca Mountain repository. Studies using buried artifacts at the Santorini archaeological site as analogs of contaminant sources would permit analyses of the rates and mechanisms of trace elemental migration in a geologic setting analogous to Yucca Mountain. The initial and boundary conditions at Santorini could be especially well defined, and the time period since burial of the artifacts (3600 years) is comparable to the period of interest in radioactive waste management.

Though Peña Blanca and Santorini provide good analogs to some processes important to high level waste containment, there are no perfect analogs. The source term and boundary conditions at Peña Blanca may be difficult to constrain closely because of the complexity of the original hydrothermal systems and subsequent alteration. Conversely, at Santorini (where the source term and boundary conditions are relatively well known) the material and elemental sources are not necessarily close analogs to spent fuel or vitrified waste forms. Nevertheless, the physical similarities between these sites and Yucca Mountain could permit identification and characterization of relevant waste form degradation and contaminant migration phenomena, and could aid in the development and validation of predictive models for performance assessments.

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