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ATOMIC ENERGY
OF CANADA LIMITED

L'ENERGIE ATOMIQUE
DU CANADA, LIMITEE

THE GEOCHEMISTRY OF HIGH-LEVEL WASTE DISPOSAL IN GRANITIC ROCKS

LA GEOCHIMIE DE L'EVACUATION DES DECHETS A HAUT NIVEAU RADIOACTIF DANS LES FORMATIONS DE ROCHE GRANITIQUE

N. A. Chapman, F. P. Sargent (editors/rédacteurs)

AECL/CEC (Euratom) Workshop
cosponsored by
Atomic Energy of Canada Limited
and the Commission
of European Communities
(Euratom)
1983 September 12-16
Minster Lovell, Oxfordshire
England

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Whiteshell Nuclear Research
Establishment

Etablissement de recherches
nucléaires de Whiteshell

Pinawa, Manitoba R0E 1L0
July 1984 juillet

ATOMIC ENERGY OF CANADA LIMITED

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Edited by

N.A. Chapman
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An AECL/CEC (Euratom) Workshop
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as part of their cooperative agreement in the
field of nuclear waste management

Held on September 12th-16th, 1983
at Minster Lovell Mill
Minster Lovell, Oxfordshire,
England

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ABSTRACT

This report describes the proceedings and conclusions of a workshop entitled "The Geochemistry of High-Level Waste Disposal in Granitic Rocks". The meeting was cosponsored by Atomic Energy of Canada Limited and the Commission of European Communities (Euratom) as part of their cooperative agreement in the field of nuclear waste management. It was held at the secluded Minster Lovell Conference Centre near Oxford in the United Kingdom during 1983 September 12-16.

Seven major topics were presented, discussed and documented. The major conclusions were:

1. Waste-form leaching and dissolution models should be superseded by solubility limits and water availability models. It is no longer appropriate to focus exclusively on the waste form; an integrated systems approach that duplicates realistic near-field conditions in a disposal vault is required.

2. Direct and significant migration of radionuclides from waste forms as colloids is unlikely under disposal condtions. Filtration will occur in the backfill and buffer, thereby providing effective retardation.

3. Most of the sorption data required to model the retardation of radionuclide migration in the geosphere are available. A thorough review is required. Further experimental work should be limited to a set of critical radionuclides (Np, I, Tc, Ra, U, Pu) and be performed for specific sites.

4. There is a need to better characterise the solid phases that sorb radionuclides and to determine their stability and kinetics of dissolution.

5. The linear programming method is proving invaluable for refining thermodynamic data bases for predicting the stability of the rock-forming minerals.

6. It is recognised that the almost complete lack of good thermodynamic data for iron-containing minerals is a serious deficiency. The need for such data was identified as a high priority for future research programs.

7. The discovery of highly saline groundwaters at many sites in Canada has suggested that these occur throughout the Canadian Shield at depths below about 500 m. This has serious geochemical implications for modelling radionuclide release and transport, and highlights the need to determine activity coefficients at high salinities.

8. Most of the components of a fully coupled groundwater flow/geochemical mass transport model are currently available. Such a model should be assembled and applied to some well-characterised site-specific problems. The computing effort will be large and could require an internationally co-ordinated program.

9. The potential effects of microbial activity on the release of radionuclides seem to be most important in the near field. This is due to the species introduced in the backfill and also due to the disposal vault (repository) being open to air during its operational phase. Future work should concentrate on characterising the biological environment of an operating disposal vault and that immediately following closure. This would be aided by studies of biological activity in existing mines and the species most likely to be introduced and flourish in backfill materials.

10. Natural analogs should be used to support all models and to justify the extrapolation of short-term observations to geological time scales. These analogs should not be restricted to only radioactive species, but should include all relevant chemical and physical processes recorded by geological observation.

The conclusions reached at this workshop have been of considerable use in determining the priorities and direction of geochemical research in Canada and Europe.

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LA GÉOCHIMIE DE L'ÉVACUATION DES DÉCHETS À HAUT NIVEAU RADIOACTIF DANS LES FORMATIONS DE ROCHE GRANITIQUE

par

N.A. Chapman et F.P. Sargent

RÉSUMÉ

Ce rapport décrit les débats et conclusions d'un atelier intitulé "La géochimie de l'évacuation des déchets à haut niveau radioactif dans les formations de roche granitique". La réunion a été copatronnée par l'Énergie Atomique du Canada, Limitée et la Commission des Communautés Européennes (Euratom) dans le cadre de leur accord de coopération dans le domaine de la gestion des déchets nucléaires. Elle a eu lieu au Centre de conférences Minster Lovell, retiré, près d'Oxford au Royaume-Unit des 12 au 16 septembre 1983.

Plusieurs sujets majeurs ont été présentés, discutés et documentés. Les conclusions principales ont été les suivantes:

1. Il faudrait remplacer les modèles de lixiviation et de dissolution des formes de déchets par des limites de solubilité et des modèles de disponibilité d'eau; il ne convient plus de concentrer les efforts exclusivement sur la forme des déchets; il faut une approche à systèmes intégrés qui reproduit les conditions réalistes existant dans le voisinage immédiat d'une enceinte d'évacuation.

2. La migration directe et importante des radionuclides à partir des formes de déchets sous forme de coloïdes est improbable dans des conditions d'évacuation; la filtration se produira dans le remblai et le tampon et assurera ainsi un ralentissement efficace.

3. La plupart des données de sorption nécessaires pour modéliser le ralentissement de la migration des radionuclides dans la géosphère existent. Les travaux expérimentaux ultérieurs devraient se limiter à un groupe de radionuclides critiques (Np, I, Tc, Ra, U, Pu) et être exécutés pour des sites particuliers.

4. Il faut mieux caractériser les phases solides qui adsorbent les radionuclides et déterminer leur stabilité et cinétique de dissolution.

5. La méthode de programmation linéaire s'avère être d'une valeur inestimable pour perfectionner les bases de données thermodynamiques permettant de prédire la stabilité des minéraux lithogénétiques.

6. On reconnait que le fait qu'on manque presqu'entièrement de données satisfaisantes en ce qui concerne les minéraux ferreux est une chose sérieuse; on a établi que le besoin de telles données serait une priorité absolue pour les futurs programmes de recherches.

7. La découverte d'eaux souterraines fortement salines sur plusieurs sites au Canada laisse supposer qu'elles sont présentes dans tout le bouclier canadien à une profondeur au-dessous de 500 m environ. Ceci a de grandes conséquences, du point de vue de la géochimie, pour la modélisation de la libération et de la migration des radionuclides et met en lumière la nécessité de déterminer les coefficients d'activité à une haute salinité.

8. La plupart des éléments d'un modèle entièrement couplé d'écoulement d'eaux souterraines/de transport de masse géochimique existent actuellement; il faudrait assembler un tel modèle et l'appliquer à certains problèmes bien caractérisés et particuliers aux sites. Les calculs seront de grande envergure et pourraient nécessiter un programme dont la coordination serait internationale.

9. Les effets possible de l'activité microbienne sur la libération des radionuclides semblent être des plus importants dans le voisinage immédiat. Ceci est causé par les espèces introduites dans le remblai et également par le fait que l'enceinte d'évacuation (dépôt) est en contact avec l'air lors de son exploitation. On devrait concentrer les futurs travaux sur la caractérisation du milieu biologique d'une enceinte d'évacuation en exploitation et, cela, tout de suite après la fermeture. Des études de l'activité biologique dans des mines existantes et des espèces qui seraient très susceptibles de s'introduire et de se développer dans les matériaux de remblayage viendraient compléter les travaux en question.

10. Il faudrait se servir d'analogues naturels pour soutenir tous les modèles et justifier l'extrapolation des observations à court terme aux échelles des temps géologiques. Ces analogues ne devraient pas se limiter aux espèces radioactives seules mais devraient comporter tous les processus chimiques et physiques y afférents enregistrés par observation géologique.

Les conclusions auxquelles on est parvenu lors de cet atelier ont servi dans une grande mesure à déterminer les priorités et l'orientation des recherches géochimiques au Canada et en Europe.

L'Énergie Atomique du canada, Limitée
Établissement de recherches nucléaires de Whiteshell
Pinawa, Manitoba ROE 1L0
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PREFACE

Granitic rocks have been considered by several countries as amongst the most suitable hosts for a deep disposal facility for nuclear fuel wastes. Work in Canada and the European Community (notably the United Kingdom and France) has progressed considerably over the last few years towards characterising the deep geological environment in such hard, fractured rocks, and since 1980 a technical cooperation agreement has existed between the European Community for Nuclear Energy (Euratom) and Atomic Energy of Canada Limited (AECL) to facilitate the exchange of data and generally push this work forward on a common basis.

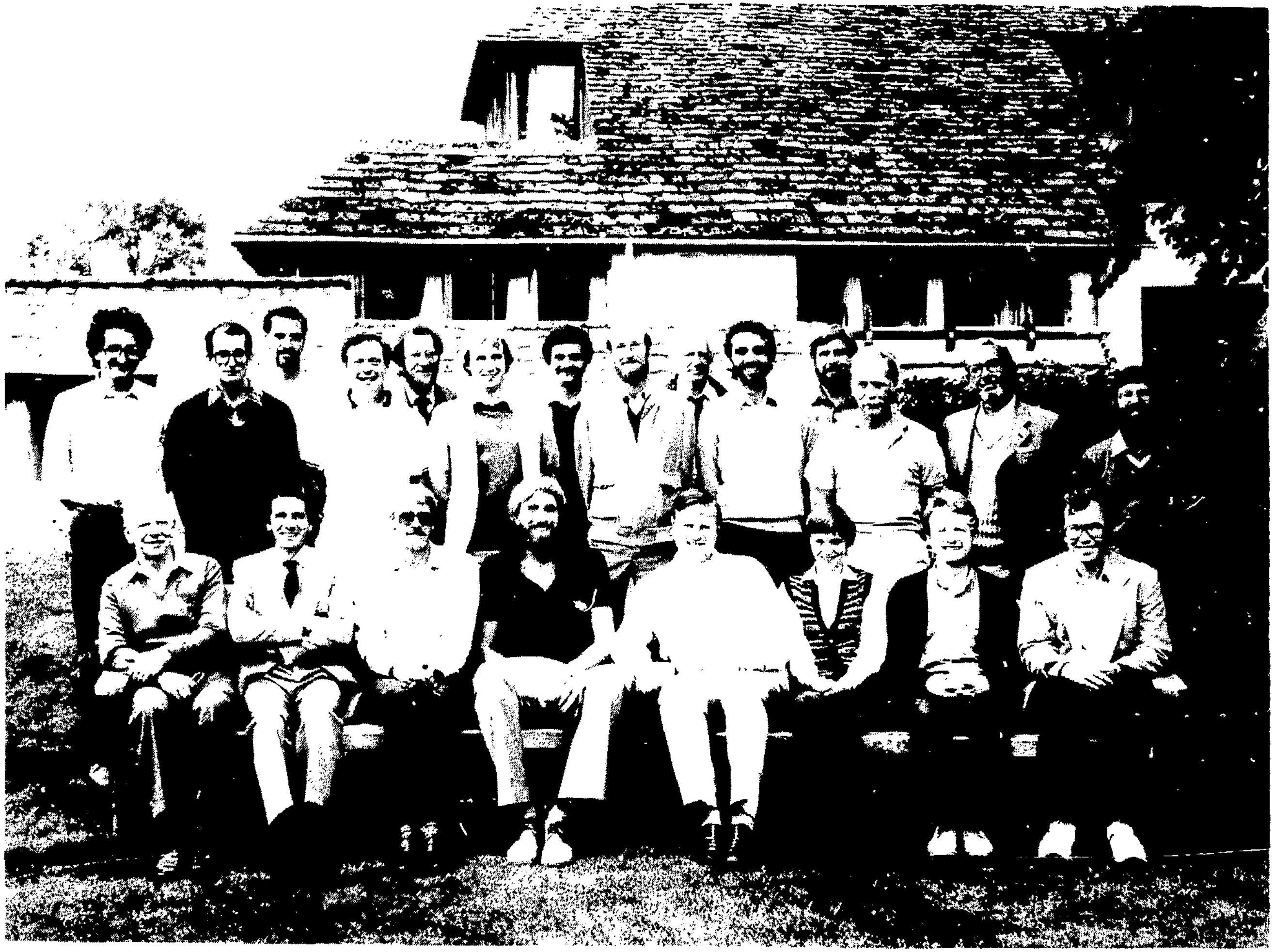
The objective of most of the research in the earth sciences area is to provide data that will either help in the design of a waste vault or form the basis for a model of its behaviour (or "performance" in containing the wastes) over long periods of time into the future. The vital data for this all-important assessment of long-term safety are in the fields of hydrogeology and geochemistry. Without detailed information on how groundwaters move through the rock and the processes whereby radionuclides are mobilised from the waste, migrate with the water and interact with the rock, it is impossible to predict the consequences of this type of disposal.

The range of influential studies under the general heading of "geochemistry" covers such diverse fields as actinide speciation in groundwaters, hydrothermal rock-fluid equilibria, cation sorption kinetics, and the chemical influence of micro-organisms in deep groundwater systems. Those involved in these researches have to contribute their individual information to a coherent model, and to understand the significance of each other's work it is clearly important to bring together such unlikely partners as mineralogists and biochemists, radiochemists and petrologists.

This workshop, the first of its kind held under the auspices of the Euratom/AECL agreeement, was envisaged as a practical means of promoting these relationships and providing a forum for intensive discussion between acknowledged experts in their fields. All participants were invited because of their specific expertise and, although the majority were from Canada or the Euratom countries, a number of participants from Sweden and the USA were invited to contribute their specialist knowledge. The discussion leaders were encouraged to prepare and present their papers in a way that would stimulate frank and open discussion of the geochemical issues. Although the concept is not new there is no doubt that "imprisoning" a group of experts together in a remote country house for a few days produces interesting results. We hope these informal proceedings reflect the usefulness of the more-or-less continuous discussion that took place, and provide a 1983 "state-of-the-art" for the geochemist studying radioactive waste disposal in granite.

Many people helped to make this workshop a success. We wish to thank S. Orlowski (Euratom), T.E. Rummery (AECL) and J. Mather (formerly with the Institute for Geological Sciences (IGS), UK), for their support throughout all stages and especially so during the initial formative period, David Savage and Julie West for the excellent job they did as the local (UK) organizers, AERE-Harwell and IGS-Harwell for clerical and logistical support, AECL, Euratom and IGS for financial support and Tony Ambrose and his staff at Minster Lovell for providing the ideal atmosphere in which to gently separate the experts from their knowledge. Finally we wish to acknowledge F. Girardi whose after-dinner speech helped set the tone of the meeting.

F.P. Sargent Pinawa
1984
N.A. Chapman Rome



Participants at the AECL/CEC(Euratom) Workshop on "The Geochemistry of High-Level Waste Disposal in Granitic Rocks" - Seated left to right: B. Skytte Jensen, A. Avogadro, J.F. Barker, N.A. Chapman, F.P. Sargent, J.M. West, D. Savage, T.J. Wolery. Standing left to right: A. Saltelli, G. de Marsily, I.G. McKinley, G.B. Skippen, D.L. Rancon, M. Apted, N. Christofi, B. Come, W.S. Fyfe, G. Bidoglio, E.S. Patera, H.J. Greenwood, F. Lanza and T.W. Melnyk. Missing are B. Allard, T.H. Brown, J.O. Duguid, F. Girardi, B.W. Goodwin, J.B. Moody and F.J. Pearson.

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SUMMARY OF THE WORKSHOP

Summarising the outcome of four days and nights of discussions between specialists might be considered a "non-trivial" task, but despite the fact that geologists are notoriously argumentative creatures, there was a very broad and firm basis of agreement as to "where we have got to, and what needs doing next".

The last few years have seen an almost continuous diversification of relevant geochemical studies. As a result of the experience gained (and in particular the outcome of sensitivity analyses of the significance of individual parameters), attention is now being refocussed on what is seen as a limited number of key issues. During the workshop, session leaders addressed these issues and provoked commentaries and discussions, which form the basis of these proceedings. Before attempting to distill their findings for this summary, it is worthwhile examining some of the more general issues for which a consensus was achieved.

Perhaps surprisingly it was felt that all the generic data likely to be needed in the fields of nuclide sorption and speciation in groundwaters are currently available. As far as the "critical" radionuclides are concerned, their limiting solubilities are sufficiently well known for the purposes of conservative, yet realistic, safety analyses, and what was needed now was to get down to some site-specific cases to assess their retardation behaviour in well-characterised systems. Almost everyone now regards the time as long overdue for applying their work to a real site.

Our ability to predict not only the results of geochemical processes, but in some cases the nature of these processes, formed an underlying thread throughout the meeting. While some processes can be considered from a kinetic viewpoint, the reaction rate constants are not always well known, and the study of natural analogues was often cited as the means of improving confidence in predictability. However, most geochemists are only really confident when dealing with equilibrium situations, and the ample geological evidence of metastability or ultra-sluggish kinetics in some of the processes of interest must be accounted for in any eventual assessments. There is no doubt that many surprises lie ahead.

By now most workers (not only geochemists, but hydrogeologists and engineers) would be only too happy to see a really thorough site assessment carried out by means of a comprehensive nuclide migration model, and to see just how their data fit into the structure, and how they compare in terms of precision with other types of data used in the model. Of the many points discussed, perhaps these two - the desire to get started on a comprehensive site-specific model, and the consensus that we had enough basic fluid chemistry data - are the most significant to emerge.

Seven topical discussion sessions were held in the workshop, introduced and moderated by an expert in that field. The discussion papers were often intentionally provocative to stimulate open and frank discussion. The following points summarise the outcome of the workshop.

(1) Mechanistic waste dissolution models ought now to be superseded by solubility limit/water availability models as the source terms for low-flow environments. It is no longer thought necessary for modelling purposes to characterise the behaviour of the waste form precisely. However, the solubility limits for individual nuclide species are insufficient, and experiments should aim to duplicate realistic near-field closed-system conditions.

(2) More emphasis should be put on characterising the solid "sorbing" phases. Better kinetic data are required to determine which phases will be the most stable retarders in the long term. As far as aqueous chemistry is concerned, we are now in a position to make a concise list of additional site-specific data requirements to facilitate experiments.

(3) Linear programming is proving invaluable for refining thermodynamic data sets, which are now available for rock-forming mineral systems. Firm efforts should be made to utilise these on large-scale realistic problems, and to enhance the quality of data for the waste elements. Sensitivity analysis should be used to identify the critical species, minerals and reactions. The lack of data for iron silicates and radionuclides is of concern.

(4) The discovery of highly saline groundwaters at many sites in Canada has suggested that these occur throughout the Canadian Shield at depths below about 500 m. This has serious geochemical implications for modelling radionuclide release and transport, and highlights the need to determine activity coefficients at high salinities.

(5) Direct releases of waste elements in colloidal form are unlikely under normal conditions of geological evolution. Filtration and re-precipitation may act as effective retardation mechanisms for some actinides, even in the near field. However, eventual dissolution equilibria involving precipitated colloidal species may be the rate-determining step in actinide migration.

(6) Most of the components of a fully coupled groundwater flow/geochemical transport model are already available, and although there are gaps in data and theory, and computing costs would be very high, we are fully justified in building such a model and applying it to some well-characterised, site-specific problems. The effort may be so large as to require a well-coordinated international programme.

(7) The majority of requisite sorption data is already available or could be very easily obtained, but a thorough review is required to collate them from the diffuse literature. Further experimental work could be restricted to "critical" radionuclides (Np, I, Tc, Ra, U, Pu) and on a site-specific basis only. Natural analogues of migration, studied critically, could aid in assessing modelling results.

(8) The potential effects of microbial activity on waste releases would appear to be dominantly restricted to the near field, and moreover to the role of introduced species. Consequently, work should concentrate

on characterising the biological environment anticipated in an operating vault and that present immediately after closure. This could be aided by determining which microbial species are present in existing mines and by assessing the importance of those likely to be introduced or flourish in backfill materials.

These conclusions have been of considerable use in determining the priorities and direction of geochemical research both in Canada and Europe.

THE VALIDITY OF LONG-TERM WASTE-FORM RELEASE MODELS

B.W. Goodwin

1. INTRODUCTION AND DEFINITION OF TERMS

Assessments of the long-term effects of nuclear fuel waste disposal in granitic rocks deal primarily with potential groundwater transport from the isolated disposal vault to the surface environment. One of the first steps in such assessments is the development of waste-form release models.

We can define a waste-form release model to be a mathematical representation of the processes that control, or otherwise affect, the release of contaminants from the waste form. This definition is somewhat all-encompassing, and in practice restrictive assumptions are often made. Typically, a waste-form release model may deal only with properties relating to the hydrothermal stability of the waste form. While this may be adequate for preliminary modelling, such models are too simplistic if synergistic effects are important. For example, nuclear fuel waste will produce heat and radiation for long periods of time. The resultant effects of the radiolysis of nearby groundwaters and the hydrothermal alteration of surrounding minerals may significantly influence the release of contaminants from the waste vault. Other external processes will also affect the design of the waste-form model, such as the volume and rate of exchange of water in contact with the waste form. In developing waste-form release models, all the simplifying assumptions should be explicitly stated, and eventually we must address the question: are the models sufficiently comprehensive?

2. MODEL REQUIREMENTS AND VALIDATION

The previous section outlined the general requirements of waste-form release models, but a few special requirements remain. These are: the models must be capable of prediction over long time scales, and they must be capable of extrapolation to a variety of geochemical environments.

The models must be capable of long-term prediction to enable quantitative descriptions of waste-form behaviour until all the contaminants have been released, or until their potential toxicity is negligible. The models must also be capable of extrapolation to enable quantitative descriptions of waste-form behaviour for conditions that may not have been encountered in the laboratory. We might anticipate, for example, very reducing electrochemical conditions in the disposal vault (modified by radiolysis and slow reaction kinetics?), but it is difficult to realize the corresponding experimental conditions in the laboratory. Uncertainties and variabilities in the geochemical evolution of groundwaters may lead to a wide range of possible environments in the vault, and we would like to be able to forecast the subsequent effects on contaminant release without resorting to a wide range of expensive experimental studies.

These special requirements for our waste-form release models impose rather exacting constraints on the validation procedures. Note that we probably cannot directly verify our models, since this implies observation of the waste forms over their anticipated lifetimes (can we "verify" using natural analogues such as OKLO for the used fuel option, or volcanic or ancient glasses for vitrified waste forms?). In general, we can only validate our models, where validate means to "support or corroborate on a sound or authoritative basis" (Webster's New Collegiate Dictionary, 1977).

The validation procedure is probably our most challenging problem. We must use caution in accepting all empirically based models, because their use in predictive or extrapolative roles is risky. Obviously theoretically based models are more desirable - but are they available?

3. MODELS AND DATA

For thermodynamically stable waste forms, simple dissolution models might be justified, if all the required data were available and kinetic effects were unimportant (or well understood). Solids such as sphene, SYNROC and uranium dioxide (UO_2) are stable and have well-defined solubilities in some geochemical regimes - do these regimes include the plausible environments for a disposal vault? Given low levels of waste loading, are these idealized solids representative of the real waste forms? Are the contaminants dispersed homogeneously throughout the waste form, and are they released congruently? Are there sufficient thermodynamic data available to account for all possible aqueous complexes? What is the effect of poorly characterized organic ligands?

Other waste forms, such as vitrified wastes and bentonite, are known to be thermodynamically unstable in a hydrothermal environment. The idealized solids will slowly alter to form new phases. If the rate of transformation is slow relative to the rate of dissolution, can we use thermodynamic models? If so, a similar series of questions arises, such as are the "pure" solids representative of the real waste forms, are the contaminants dispersed homogeneously, and are the contaminants released congruently?

If a thermodynamic model is not applicable, can we base the contaminant release on diffusional processes? Given low theoretical values of solid-state diffusion constants, is this approach realistic? What are the long-term implications of a diffusion-based model? Are these implications realistic, and can they be validated? Recent studies of the dissolution of silicate minerals have shown that the dominant dissolution process is not diffusion, but kinetically hindered surface reactions. Could similar reactions be responsible for the observed dissolution of vitrified waste forms? If this is the case, the implication is that we require a detailed understanding of the reaction mechanisms. Can we ever achieve such an understanding, and can we expect to validate such mechanisms? Can kinetic models be used reliably to extrapolate to other geochemical environments? In most cases, our models will be based on laboratory observations, and it is not immediately clear whether suitable experiments are being conducted that directly address model development. For example, a set of Gibbs energies may be required by a thermodynamic model, but are there enough data available to show that a thermodynamic model is appropriate? Limited data exist for the dissolution of used fuel, but are the experimental conditions representative of the expected conditions in the vault? Similarly, one can find a vast amount of data describing the dissolution of different glasses, but in many cases these data are directed at studies of relative durabilities in the short term. For any single glass, there is a limited amount of data available that can be used to develop a suitable long-term dissolution model.

Is there any way of accelerating the experimental studies, so that we can obtain long-term data in a finite time? High-temperature studies provide one possible approach, but the results must be used with caution, because reaction mechanisms and stability fields could change with temperature. Are there any other techniques available? Are natural analogues a possibility?

4. SAMPLE MODELS

The following discussion describes two postulated waste-form release models, one for used UO_2 fuel, and one for a very durable (and somewhat hypothetical) sodium borosilicate glass. Note that they are intended for use in long-term assessments, and are assumed to be condensed and simplified from more detailed understanding. Do these, or any other models, address all of the questions raised above?

One implicit assumption in both models is that the long-term dissolution of the waste form is congruent. Since used fuel and glass are both reasonably durable in a hydrothermal environment, the assumption implies that the original waste form will persist for long periods of time. Note that, as used here, congruent dissolution occurs when the components of a solid dissolve in the same proportions as are present in the solid phase. This definition includes "apparent" incongruent dissolution, where congruent dissolution is followed by mineralization or precipitation from the aqueous phase, so that experimental observations may show nonstoichiometric concentrations in the leachant. Incongruent dissolution, on the other hand, means the selective dissolution, or leaching, of some components from the parent solid. Both models contain an incongruent step, but it is assumed that incongruent dissolution is important only for short time frames.

The postulated waste-form release model for used fuel assumes that contaminant release can be represented in terms of two chemical processes. The first process is incongruent, reflecting the inhomogeneity of a used fuel matrix. Some radionuclides, such as ^{129}I and ^{135}Cs, are relatively volatile at reactor operating temperatures, and a small fraction of their inventories migrate to the cooler fuel-sheath gap. These radionuclides are assumed to be entirely released at the instant that groundwater penetrates the fuel sheath, and this component of the model is described by a parameter known as the "instant release fraction" - the fraction of volatile fission products that accumulates outside the fuel matrix.

The second process is congruent, reflecting the stability of UO_2. It is assumed that contaminants contained within the fuel matrix are released as the fuel dissolves. The required parameter here is the solubility of UO_2. Some implicit assumptions are that UO_2 is the thermodynamically stable phase, that UO_2 can represent used fuel, and that a geochemical pump is not established (where uranium dissolves from the fuel, releasing contaminants, then precipitates nearby to allow more uranium fuel to dissolve).

The postulated waste-form release model for sodium borosilicate glass also assumes that there is an initial period of incongruent dissolution. In this case, the incongruent release may be due to the inhomogeneous distribution of contaminants, and the initial fast reactions between groundwater and the surface species on the glass. The required parameter is the "instant leach fraction", which describes the fraction of contaminants that are selectively released in a short time following exposure of the glass to the groundwater. This parameter could also be considered to be a product of the effective glass surface area and the effective leach depth.

For longer periods of time, other contaminants in the glass are assumed to be protected by a silica-rich leached layer, and subsequent release is controlled by the slow kinetics of dissolution of a silicate framework. This process is described by an "effective" glass solubility, with congruent release of the contaminants. Solubilities and waste loadings are higher for glass than for used fuel, and some elements may be supersaturated; therefore, elemental solubility limits are imposed.

This model contains many more implicit assumptions than the used fuel model; for example, it assumes that contaminant release is controlled by surface reactions, that a silicate framework solubility exists, that the mechanism of dissolution is not altered (by auto-catalysis effects?), and that processes such as diffusion or solid-state transformation are not important.

5. SUMMARY

Waste-form release models describe all the processes that affect the release of contaminants from all the waste forms emplaced in a disposal vault. The models must be capable of prediction to long time scales, and of extrapolation to a variety of geological environments. These requirements mean that the resulting models must be based on a sound understanding of the processes involved, so that model validation can be achieved.

Currently available models are often simple in scope, and are based on concepts such as thermodynamic equilibrium, diffusion and/or chemical kinetics. Most models are still in the developmental phase and require further laboratory and field data for their validation.

Two models have been outlined - one for used fuel and one for vitrified fuel recycle waste. The models are conceptually simple, and very similar, and may serve as a starting point for further discussion.

DISCUSSION

A number of issues were raised during the review of the discussion paper. The definition of waste-form release models was generally accepted. General categories for waste-form release models were identified as kinetic models, thermodynamic models, and irreversible thermodynamic flow models. There was general agreement that waste-form release is, however, only one of the reactions occurring in a nuclear waste vault that must be evaluated and included in an overall waste package release model.

The definitions of congruent and incongruent dissolution and apparent incongruent (leaching) were accepted. Discussion concentrated on review of two major controlling dissolution mechanisms; mass transport via diffusion (controlling incongruent dissolution) and surface-controlled reactions. It was stressed by a number of researchers that both of these mechanisms, as well as other mechanisms contributing to dissolution, occur simultaneously. The relative importance of one process with respect to the other will be determined by the ratio of the rates for these mechanisms. A general conclusion reached was that, while diffusion may be important, surface-controlled kinetics is probably equally as significant. The term "leaching" is, therefore, too specific for describing overall dissolution, and its use was generally thought to be misleading and inappropriate for the description of long-term (>28 days) dissolution of both crystalline and glass waste forms. The use of the terms "leaching" and "leachability" should be abandoned in favour of the more general term "dissolution" in describing the general release of contaminants from waste forms.

While it may not be feasible to deduce a complete chemical kinetics mechanism describing the dissolution of glass and subsequent release of radionuclides, it may be important to understand these processes in greater detail than currently exists. In this regard, experimental studies should evaluate the effects of surface preparation techniques, initial solution chemistry and radiolysis, as well as temperature, redox potentials and pH, on dissolution behaviour.

One important issue raised was whether waste-form release models based on dissolution of the waste form are justified, since some experimental results suggest that it is the presence of secondary alteration products that control radionuclide release. It was generally concluded that both dissolution of the primary waste form, and dissolution of a secondary phase, could dominate radionuclide release. This conclusion is not surprising, given the wide range of elements contained in the waste, and the wide range of possible hydrological flow regimes.

The release of highly soluble elements, such as sodium and iodine, will likely be controlled by dissolution of the primary waste form. Less soluble elements, such as the actinides, will likely form secondary solid phases, which will control their release. The transition from release controlled by the primary waste form to that controlled by secondary phases will depend on the hydrological flow in the vicinity of the waste form. At high flow rates, the rapid removal of dissolution products could inhibit the formation of secondary solid phases for all but the most insoluble of elements. At very low flow rates, where transport is mostly by diffusion, for example, local saturation may occur, leading to the formation of a variety of secondary solid phases, which could then control the release of all but the most soluble of elements.

Solubility models were divided into true equilibrium models, in which the most stable assemblage of alteration phases is assumed to form, and metastable equilibrium models, in which an assemblage of metastable phases is assumed to form. While it would be easier to individually measure solubilities for the most stable solids for each radionuclide of interest, results of waste-form tests have shown that the formation of metastable radionuclide-bearing solids is more common. Metastable solids also have higher solubilities than stable solids, so it is important to characterize these solids to provide conservative radionuclide concentrations. Because the actual metastable phases that form will be functions of temperature, solution composition, the presence of other radionuclides, and other site-specific test parameters, solubility studies on single radionuclide phases is not a recommended approach for obtaining the necessary data for metastable equilibrium models. Tests performed with actual waste forms under expected vault conditions were recommended as providing the most relevant and defensible data for models of waste-form release. However, interpretation of data may be facilitated by solubility studies of a simple system under relevant conditions.

Some recommendations for experimental studies include detailed analysis of solution concentrations of <u>all</u> dissolved species, including pH and anions. Results from other discussions suggest that it may also be important to characterize more fully those elements released as colloids. These studies will give information on long-term steady-state concentrations of sparingly soluble elements, and may also provide more relevant data for chemical kinetics models.

One important note was that attaining steady-state or solubility concentration limits for some components does not imply that dissolution has stopped for all components. The observed constant concentration of some component may be a consequence of steady-state dissolution and precipitation, with the implication being that some other (unobserved) component may be steadily increasing in concentration. It is also important to continue with attempts to characterise the new solid phases. Although these experiments and analytical requirements are not trivial, they are very important in the deduction and defence of a suitable waste-form release model.

It was also noted that synergistic effects cannot be ignored. Groundwater preconditioning and the presence of nearby container or buffer/backfill material, for example, are known to have a strong influence on the resultant release rates of contaminants and the nature of alteration phases. In some cases, the very slow transport of components away from the waste form may dominate the release of radionuclides. A compacted medium such as bentonite, for example, could control the rate of transport of silica from the waste form, thereby having an overall control on the release of radionuclides from a vitrified sodium borosilicate waste form. The release of slightly soluble components, such as the actinides, may also be controlled by solubility equilibria at the interface between waste form and backfill/buffer, and their subsequent diffusion. These effects imply that a further series of complex 'system-type' experiments, which are more representative of waste forms in a 'real' waste package and vault environment, is warranted.

In summary, the following major conclusions were drawn:

- Congruent and/or "apparently" incongruent dissolution processes are likely to dominate dissolution for most waste forms over long (>28 days) time periods at relevant vault conditions. Use of the term "leaching" and diffusion-based models for dissolution control should be abandoned in favour of a broader, more general approach to dissolution modelling.

- Congruent and "apparently" incongruent dissolution may occur simultaneously for all radionuclides. The relative rates of these processes may change as a function of time, temperature, bulk composition and other parameters.

- Under low groundwater flow conditions, equilibrium or metastable equilibrium processes likely control groundwater concentrations for those radionuclides that are slightly soluble. Dissolution of the waste form will control only those elements that are not incorporated in secondary solid phases.

- Groundwater flow rate may lead to a variety of effects on waste-form release, and should be investigated as an adjustable experimental parameter.

- Tests with actual waste forms under expected vault conditions, and in the presence of relevant barrier materials, are necessary. Solubility tests on single radionuclide-bearing phases in isolation are not recommended for obtaining equilibrium or steady-state concentration data, although tests of this type under appropriate conditions may help to interpret more complex results.

- Detailed characterization of starting materials is important. Complete determination of solution composition and reaction products (including colloids) is also required to ensure adequate evaluation of test results.

- Obtaining a steady-state concentration for the major components of a dissolving phase does not imply that dissolution stops. There could exist a balancing of dissolution and precipitation rates, resulting in a zero net increase in concentration of major components. Incorporated trace elements or radionuclides, however, may continue to be released.

THE APPLICABILITY OF EQUILIBRIUM MODELS, KINETIC DATA AND THE USE OF LOW-TEMPERATURE EXPERIMENTAL DATA

B.S. Jensen

I take for granted that the main theme of our present discussion should be concerned with the behaviour and fate of radionuclides in a granitic environment, and from a safety point of view we would be satisfied if we could demonstrate that they either do not move or, if they do, that they become excessively diluted during their migration.

The plans for the disposal of radioactive waste leave very little time for the testing of the long-term performance of a repository, so the evaluation of the hazards involved in the operation relies heavily on model calculations.

Granite is basically a wet formation, where radioactive nuclides eventually released may move with groundwater along a network of fractures. The migration of radionuclides will be retarded by ion-exchange or other adsorption mechanisms and complex-formation or other reactions in solution may conversely enhance their migration [1]. The question of our understanding and modelling of these phenomena is the main theme of this seminar.

Much effort has been expended in the laboratory in recent years to characterise the behaviour of radionuclides in solution and in contact with different solid mineral phases. Based on these "equilibrium" observations numerous model calculations have been performed which in some way display the "expected" behaviour of released radionuclides in the environment.

A brief dive into geochemistry will give a non-specialist the first impression that an enormous amount of data and chemical information has been collected over very many years and that not much is left for investigation.

A second impression could be that the existing data often seem to lack consistency and that only rather vague conclusions result from their analysis. Results most often come out as patterns or trends and not as the exact numbers, which most often arise from laboratory investigations.

This unsatisfactory situation has to some extent been relieved by the outstanding efforts made by several scientists during the last decades, to apply the concept of local equilibrium in the interpretation of diverse observed geochemical phenomena (weathering sequences for example).

The idea of local equilibrium implies that on the "large scale", which may be as small as distances measured in millimetres, chemical equilibrium may not be attained.

Minerals formed by solidification from a molten magma will seldom be thermodynamically stable at low temperatures in contact with water, and one may envisage that they immediately start to degrade in contact with water, and that most mineral surfaces are covered by layers of weathering products at different stages of crystallisation.

Assessment of these processes has resulted in the construction of several more or less elaborate computer programs, which are able to rapidly produce numbers describing expected equilibrium compositions of diverse solid and liquid phases, provided the relevant thermodynamic data are available. Furthermore, the programs may often be used to describe sequences of reaction products which may arise when an irreversible reaction proceeds.

Very often the results of these computations look very reasonable, but unfortunately the analytical proof that the result is correct is hard to achieve. However, the frequently quoted observation, that groundwater is over- or under-saturated with regard to even simple solids, indicates that some other factors need to be considered.

Many other points could be raised which ought to force one to hesitate in postulating that a detailed knowledge exists of what is actually going on in a groundwater system in contact with solids.

Some obvious complications could be:

(a) there is not adequate mixing of large volumes to secure identity of conditions in all groundwater samples,

(b) groundwater flow is fast compared to dissolution/precipitation reactions, and simple equilibria may not be established, but rather a series of stationary states,

(c) equilibria (or stationary states) may be determined by metastable solid phases, which have not yet been properly characterised, and not by the well-defined hydrous aluminosilicates normally considered in such calculations,

(d) the phenomena of solid solution may not have been properly taken into account,

(e) not all equilibria in solution have been properly characterised.

The realisation that the matrix within which a radionuclide migrates is a very complicated system, which is not fully understood or at least not comparable to a test tube, must influence our ideas about the migration phenomena.

A radionuclide released to the environment becomes chemically a part of the system, taking part in the chemical processes its chemistry favours. It will take part in complex-forming reactions, ion-exchange, be incorporated in solid solution etc., like all other elements found in the environment.

All the reservations we have been forced to express regarding equilibrium calculations on groundwater systems will therefore also be valid for the traces of radionuclides migrating away from a repository.

The weathering of diverse minerals has been studied in several cases, always showing the same general pattern. At first one observes a quite rapid, (i.e., within a few hours,) congruent dissolution of the mineral, where the increase in concentrations of elements in solution is directly proportional to their abundance in the mineral. At a later stage, the dissolution becomes incongruent, i.e., new solid phase(s) build up as weathering progresses. From an analysis of the concentration changes in solution, an aluminosilicate of continuously varying composition has been postulated as the primary weathering product of common minerals [2]. At later stages and at higher temperatures the formation of the conventional weathering products like zeolites and clay minerals has been demonstrated.

The primary weathering product could be similar to the amorphous aluminosilicate gels formed in the primary stages in the synthesis of zeolithes. This gel is known to possess ion-exchange properties, as will any solid solution of hydroxides of elements of differing valency. It is probable that this primary weathering product is the solid phase adsorbing trace-elements, and some recent observations may support this suggestion.

The major minerals in granites are aluminosilicates, and one should therefore expect that the primary weathering product of many minerals will have approximately the same composition and properties, <u>if equilibrium conditions operate</u>.

Studies on the adsorption of elements on selected mineral surfaces [3,4] have in fact demonstrated that adsorption of Am^{3+} is most effective on the minerals that are known to weather readily like augite, hornblende, biotite, anorthite, etc.

Furthermore, the extent to which adsorption is dependent on pH is at a maximum where the postulated amorphous aluminosilicate is the least soluble [2,4].

It could, therefore, be that the bulk minerals in granite do not possess adsorption capacities by themselves or at least only to a minor degree, but that the observed adsorption phenomena must be related to covering layers of their primary amorphous weathering products.

The ultimate weathering products (clay-minerals, etc.) have rather large adsorptive capacities and will retard migration by themselves.

It has been realized by most researchers that a given K_d value is only a single measuring point from a complicated relation which describes the variation of adsorption of radionuclides under varying conditions.

The prediction of the fate of a radionuclide with time and under varying conditions can only be made if this relation is reasonably well known.

Several studies have been performed describing the variations of K_d with pH, for example, but how useful are these measurements - do they really correspond to conditions found in nature?

Probably not. Minerals are by no means unreactive components and experiments conducted at different pH values may have resulted in different degrees of weathering, thereby changing the system being measured. Similar artificial pH jumps do not occur in nature, which in most cases exert a strong buffering effect.

The experimental system is therefore undergoing changes. It has seldom, if ever, been characterised, and no attempts have been made to separate reversible and irreversible mechanisms in adsorption experiments, although numerous measurements have demonstrated that the overall process is seldom reversible, i.e., adsorption and desorption do not reach the same equilibrium.

Nature does not supply pure components and we have to realize that when we are studying adsorption onto "pure minerals", we are actually studying the adsorption onto mixtures.

If we neglect kinetic effects, we can describe adsorption simply by ion-exchange mixtures.

The K_d value measured on a mixture of two adsorbers, with specific ion-exchange capacities C_1 and C_2, and each showing distribution coefficients $K_{d(1)}$ and $K_{d(2)}$ with a radionuclide can be expressed as

$$K_d = \frac{xC_1K_{d(1)} + (1-x)C_2K_{d(2)}}{xC_1 + (1-x)C_2}$$

where x is the weight-fraction of component 1 in the mixture.

Figure 1 shows a series of calculations for a binary mixture of a component with (1) high selectivity for Sr^{2+}, and (2) one with a low selectivity. Furthermore the Sr^{2+} concentration in the aqueous solution is varied, to demonstrate the saturation effect.

The curves display that by tracer experiments one may obtain data showing a retardation effect one to two orders of magnitude larger than with macro-concentrations.

One must therefore be careful not to extrapolate too far on the basis of published K_d values, which in most cases have been determined at tracer concentrations.

Conversely one may consider minerals with impurities or centers that show very high selectivities for almost any element, although of very small capacity, such that once a radionuclide has been diluted to very low concentrations, it will be very strongly adsorbed.

The effect of slow adsorption reactions on the migration behaviour of a radionuclide is very pronounced if the velocity of convective flow is comparable to the velocity of adsorption [1]. The curves calculated in Figure 2 demonstrate that the species tend to be spread out over the whole migration path by the mechanism, which may be named kinetic dispersion.

Recent experiments at Riso (Denmark) on the adsorption of Eu on pure NaCl from a saturated NaCl solution, indicate an equilibrium K_d value of about 40, which, however, is established slowly giving rise to elution patterns like those mentioned above. Similar patterns may underlie many of the experimental distributions of concentrations in other media.

Finally a comment on the question of the applicability of equilibrium data put forward in the title of this session. I feel that we are in any case forced to apply equilibrium calculations, because their basis is relatively wellfounded and they are relatively easy to apply, but we should always be aware of the limitations of our models. Our kinetic data are based on much less firm evidence and their application in calculations should rather be as corrections indicating trends away from equilibria. Within the relatively narrow temperature ranges encountered even in the near-field zone, I feel confident that, provided that the relevant experimental measurements have been made, the thermodynamic data will be of sufficient quality to allow good calculations of equilibrium concentrations at higher temperatures.

An increase in temperature will, however, favour stable species at the expense of metastable species. Adsorption measurements performed at lower temperatures may therefore concern a different substrate than that functioning as adsorbent at higher temperatures.

When considering processes in solution, the equilibrium calculations are straightforward, and provided the input data are relevant, the speciation scheme will be largely correct.

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DISCUSSION

In addition to the discussion paper, the successful derivation and validation of an expression describing multi-element ion-exchange on a simple synthetic material was presented, as an example of a mathematical expression that could be used in modelling.

The hope that similar expressions can be derived when considering complex rock/soil components was discussed, using the transformation of kaolinite to gibbsite as an example. It was concluded that, contrary to the successful example mentioned above, the transformation of minerals during the experiments may influence the experimental data such that no simple general adsorption relation can be derived.

A few calculations of the relative amounts of weathering products from a single mineral, and the same mineral together with an additional mineral species, demonstrated that the relative amounts of weathering products not only change, but that new species may replace others. The calculations were based on the linear programming technique of minimising the total free-energy of a mixture of oxides by their reaction to other mineral species. The database was that published by Helgeson.

In the following discussions, the main emphasis was placed on the applicability of thermodynamic calculations to waste isolation problems.

There seemed to be some disagreement on how much attention should be paid to the properties of the solid phase(s) whereas the speciation in the aqueous phase was considered by all as an important topic.

The discussions digressed to general geochemical discussions concerning the coincidence between geological observations and computer predictions.

Among factors that could be the cause for some observed discrepancies, kinetic effects were generally considered the most probable. Studies on dissolution rates, which are going on at several laboratories, may improve the situation, but doubts were also expressed about the usefulness of the results of these clean studies in the interpretation of what is actually happening in groundwaters.

The problem of the formation of metastable mineral phases instead of the thermodynamically most stable phases was discussed. The objective is not so much to calculate their formation or abundance, as to find criteria for omitting the stable phases from the calculations. In this choice, kinetic information will certainly be useful. Temperature may be an important factor because by increasing the temperature, kinetic rates are generally accelerated, possibly speeding the transition of metastable phases to stable phases. Under near-field conditions the transformation of metastable species to stable should be more probable than in the far field.

Regarding the usefulness and applicability of these thermodynamic calculations, it was mentioned that some of the minerals formed by weathering were in fact ion-adsorbers, and that the calculations could predict formulations for "active" backfilling composition, which when exposed to groundwater would weather to ion-adsorbing species, at the same time undergoing an expansion thereby improving the sealing of the repository.

A general problem in modelling and model validation, apart from poor input data, is incorrect or incomplete ideas about the chemical reaction that has to be considered. The literature is full of data that have been calculated based on too simplified assumptions, and whose application in calculations can give rise to grave errors, which often pass unnoticed except when sought directly.

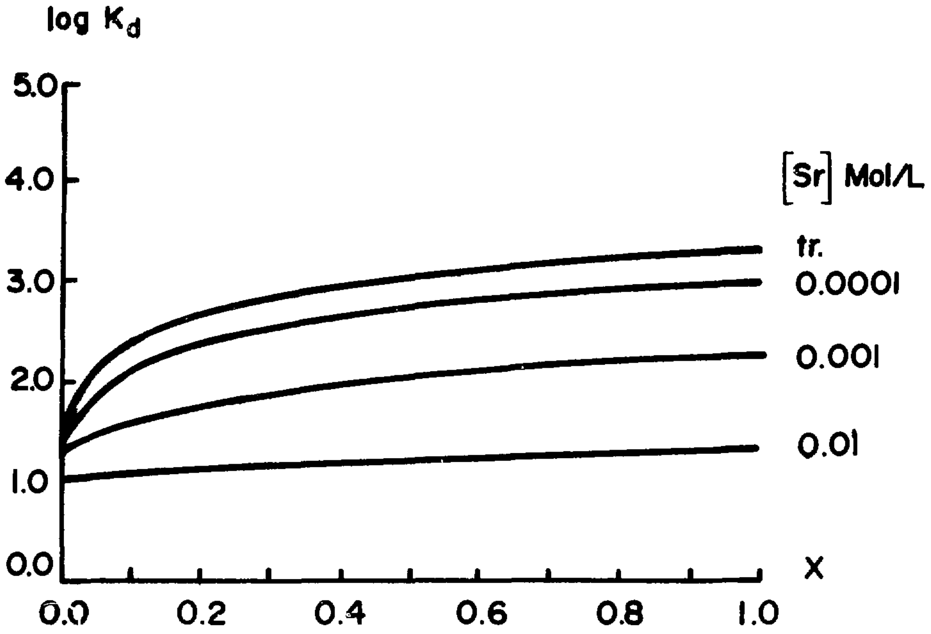

FIGURE 1: Calculated Curves Over the Variation of Log K_d for Sr^{2+} in Competition with Ca^{2+} Plotted Versus the Weight Fraction of a Highly Selective Exchanger in an Exchanger Mixture. The effect of variation in the total Sr^{2+} concentration is also displayed.

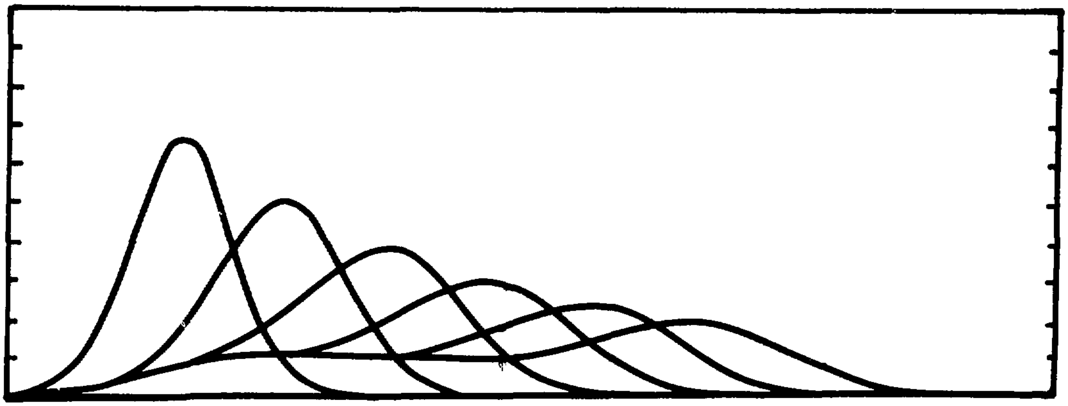

FIGURE 2: The Effect of Slow Adsorption Kinetics on the Dispersion of a Solute in Excess of the Sorption Capacity. Dimension arbitrary.

THERMODYNAMIC DATA ANALYSIS USING LINEAR INEQUALITIES

T.H. Brown and H.J. Greenwood

In recent years, petrologists have increasingly turned to the results of phase equilibrium studies to estimate thermochemical data and mixing properties of solids, gases and solutions. Most estimates (e.g. Haas et al., 1976 and 1982) are obtained by linear regression of phase equilibria data. This method of treating the data tacitly assumes that the equilibrium conditions (T,P,X) are known, by producing fits designed to be as close to as many of the estimated equilibrium points as possible. Most phase equilibria techniques do not, however, identify the equilibrium conditions of a reaction, only the relative stabilities of the product and reactant assemblages. Thus, although the equilibrium condition is expressed as

$$\mathrm{WG(reaction)} = 0, \tag{1}$$

experimental results convey only information regarding whether the sign of WG(reaction) is positive or negative. Thus a more realistic criterion for the analysis of experimental data comes from

$$\mathrm{WG(reaction)} = \mathrm{G(products)} - \mathrm{G(reactants)} \tag{2}$$

which may be positive or negative, but which is never zero in an experiment in which some progress occurs.

In recognition of this situation, Haas et al. (1982) use weighting factors in order to "reduce(d) the tendency of the regression to settle on the midpoint of a (experimental) bracket". In considering data for coexisting clino- and ortho-pyroxenes, Lindsley et al. (1981) found that only very small ranges of compositions within certain brackets were consistent with the constraints imposed by the rest of the data. They performed repeated least-squares regressions, "adjusting compositions at each cycle according to a strategy designed to reduce the residuals" (pg. 166).

A more rigorous mathematical treatment of phase equilibria data is obtained with the use of linear programming, as outlined by Gordon (1973; 1977) in his treatment of solid-fluid reactions. The technique of linear programming has already been described in the geologic literature (e.g. Greenwood, 1967; Day and Halbach, 1979; Day and Kumin, 1980; Hammerstrom and Brown, 1983; Berman and Brown, 1983). It consists of an algorithm for continually improving an objective function while maintaining feasibility, i.e. consistency with the sense of all inequality constraints (Figure 1). In relation to phase equilibrium studies, inequality constraints can be written for each half-bracket, i.e. each determination of the conditions where either reactants or products are stable. In contrast to linear regression, which provides a unique fit that tends towards the midpoints of experimental brackets while not ensuring consistency with all brackets, linear programming ensures consistency with all experimental data, but provides a range of solutions, which can be unique only for a given objective function (Figure 1). Gordon (1973) uses the WG(reaction) and WS(reaction) as objective functions, although any property of a phase or combination of such properties could be used. In addition, some linear programming computer packages allow use of non-linear objective functions, so that a solution similar to that produced by regression (but always internally consistent with all data) could be achieved (Gordon, 1977).

In contrast to regression analysis, linear programming offers the advantage that a model can be constrained by the T,P,X position of a non-stoichiometric liquidus mineral, without knowledge of the activity-composition relations of the mineral. Reference to Figure 2 shows that the "liquid stable" constraint represents the upper limit for the stability field of any liquidus mineral. Since the reduced activity of a non-stoichiometric phase expands its stability field (relative to the stoichiometric phase) to that observed experimentally, calculation of the "liquid stable" constraint assuming stoichiometry are valid for both stoichiometric and non-stoichiometric minerals.

In the testing of thermodynamic data sets, one must not only compare the predicted properties with the input data, but must also calculate all possible reactions (if practical) to examine the consequences of the entire data base. Any set of thermodynamic data should not be viewed as the final or absolute set of properties that can or will be generated by the linear programming method. When new experimental data become available, these data can be added to the existing data base and all of the data retested for internal consistency.

Every new item of experimental data has the potential to further delimit the thermodynamic maxima-minima ranges of the properties of one or several of the phases and, ultimately, to change the predicted phase relationships. For this reason it is essential that all of the experimental data, old and new, be included in the analysis calculation and that the new data are not simply "tacked on" to the existing thermodynamic properties. This process of updating the thermodynamic data set and calculating new phase relationships can be completed in a relatively short period of time because of the power and efficiency of their linear programming method.

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DISCUSSION

The session was introduced by presentations by H.J. Greenwood and T.H. Brown, emphasizing the derivation of internally consistent sets of thermodynamic properties from primary data including calorimetry, equilibrium, and "bracketing" phase equilibrium data. Many examples were presented to emphasize the applications of linear programming analysis to this problem. Data have been obtained and fully analysed for 50 phases in the $Na-K-Ca-Al-Si-O-H-CO_2$ system, and all stable equilibria computed and plotted. A new heat capacity function showing better high temperature limiting behaviour has been fit to the existing calormetric data for all the phases.

The first part of the discussion focussed on the ability of the linear programming method to converge to a set of internally consistent parameters that are consistent with all the relevant data, and to identify experimental data that cannot be reconciled with the main body of a data set. Brown and Greenwood described the use of the method to help in identifying "possibly bad" experiments, followed by scrutiny of the primary data for evidence that it could be rejected from the analysis. This led to remarks by Fyfe, Skippen and Jensen on the importance of proper phase-characterization to any consistent data-set. Ill-defined materials, or incorrectly identified materials may lead to incorrect or totally inconsistent results, and many experimental starting materials may crystallize metastably to phases that are not easily removed, preventing the examination of stable equilibria.

Discussion then moved toward questioning the usefulness of thermodynamic modelling, especially as it relates to regions outside of the thermal anomaly caused by a radioactive waste disposal vault. McKinley suggested that these "far-fields" could be treated as being unaffected, and that existing in-filling phases could be used to predict that nothing much would happen. Several speakers replied that it is not obvious whether pore-fluids, 'pumped' by a thermal anomaly, would cause enlargement of pores with an increase of permeability, or filling of pores with a decrease of permeability. Geochemical modelling, using a good data base and a fully coupled analysis of fluid flow, heat flow and chemical equilibria seems a necessary first step in an analytical treatment of this problem.

Further discussion focussed on the problems expected in expanding the thermodynamic data base to include dissolved aqueous species. Particularly difficult will be the assignment of appropriate heat capacity equations to the species and the reliable identification of species actually present in the data used for analysis. Solubility studies that report only macroscopic or stoichiometric properties will have to be fit to equations of state involving dissolved species that have not been directly identified, leaving room for uncertainty in results inferred by computation.

The group expressed the opinion that the data treatment presented by Brown and Greenwood is the best available, and urged early publication. No other set of data is known to be fully consistent.

The moderator of the session urged most strongly that now that we have such a powerful set of data, which has been analytically coupled to general equations of heat flow, permeability, and chemical reaction, we must somehow find the funds to perform the computations. This cost will not be trivial for a three-dimensional analysis of useful size, but since that is the main purposes of collecting and analysing the data in the first place, it would seem wasteful to settle for a limited, one-dimensional, two-component treatment when the tools exist for a full study. We are almost ready to begin full geochemical modelling.

These discussions also revealed a major weakness, namely the complete absence of data for the iron-containing minerals in granites such as chlorite, biotite and amphibole.

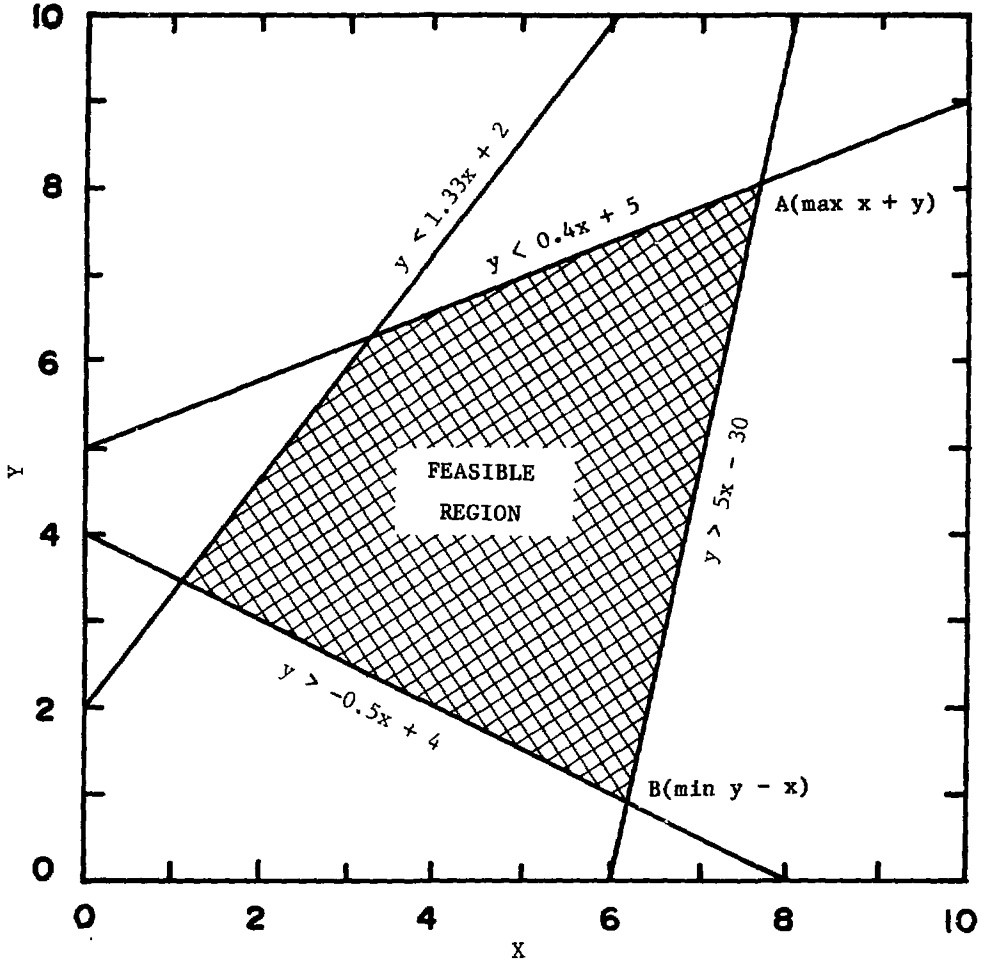

FIGURE 1: Two-Dimensional Linear Programming Problem, Showing Feasible Region Defined by Four Linear Constraints, and Optimal Solutions (A and B) for Two Different Objective Functions

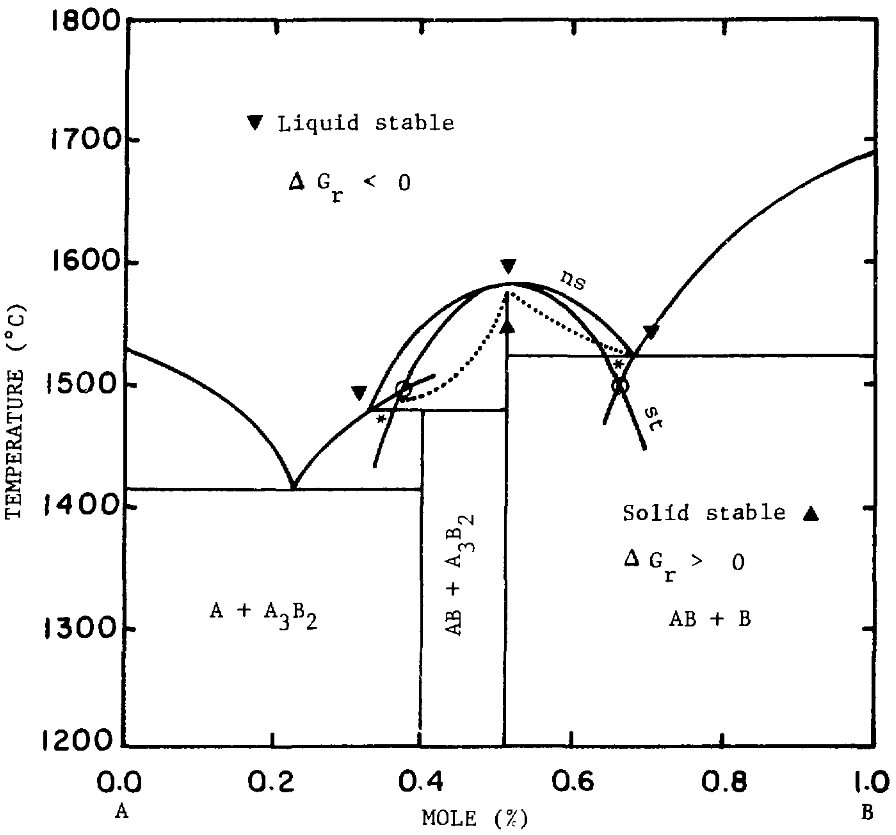

FIGURE 2: Binary Phase Diagram Showing T, X Coordinates for Liquidus Constraints. Incorporation of estimated experimental errors in temperature and composition yield the position of 'liquid stable' and 'solid stable' constraints. The reduced activity of nonstoichiometric A_3B_2 causes the experimentally determined liquidus (solid line labelled 'NS') to occur at higher temperatures than that calculated for stoichiometric A_3B_2 (thinner solid curve labelled 'ST'). Note that the position of the 'liquid stable' constraints is consistent with the position of the stoichiometric liquidus, while two 'solid stable' constraints (stars) are inconsistent with the stoichiometric liquidus. Also notice the circled intersections which show that, for the stoichiometric diagram, the reaction point occurs at a higher temperature and the eutectic at lower temperature than the experimentally determined invariant points.

THE ROLE OF COLLOIDS AND FILTRATION ON RADIONUCLIDE RELEASE AND MIGRATION

A. Avogadro

1. INTRODUCTION

Knowledge of the physico-chemical forms of radionuclides leached from conditioned nuclear wastes is rather scarce. Experimental studies carried out so far with vitrified waste leachate have demonstrated that radioactivity is present in the water phase in soluble as well as in colloidal form.

In order to elucidate the migration behaviour of the radionuclides eventually leached from a nuclear waste repository, a better understanding of the released species and of their interaction with the geologic media is needed.

Other sections of these proceedings deal with the thermodynamic and kinetic aspects of soluble species. What is discussed here concerns the formation, evolution and transport mechanisms of the colloidal fraction.

The source term considered is a borosilicate glass containing high-level waste originating from fuel reprocessing.

2. RELEASE OF COLLOIDS FROM THE GLASS SURFACE

In the release of the different radionuclides from borosilicate glasses, a prominent role is played by the leaching rate of silicon. Silicon dioxide represents the skeleton of the glass matrix and its release rate establishes the rate of degradation of the glass. It is presumed that the leaching of silicon will be controlled, in a closed system, by the saturation concentration of dissolved silica.

Laboratory experiments have been performed in order to investigate the leaching rate of glasses with time; weight loss is normally taken as an index of the leaching. Saturation is considered attained when no more weight variations are encountered.

The analysis of silicon content in the leachate has confirmed that saturation is reached; however, the silicon concentration is found to be well below the maximum concentration of amorphous silica [1,2]. In order to explain this discrepancy either reprecipitation of hydrated crystals or an extremely slow increase of silicon content in the solution has to be postulated.

For the other elements composing the vitrified waste, if we compare their leaching rate (Ki) and maximum concentration in the leachate (Ci) with those of silicon (K-Si and C-Si) three cases can be defined [3]:

1. elements for which $Ki > K\text{-}Si$
2. elements for which $Ki \leq K\text{-}Si$ and $Ci > C\text{-}Si$
3. elements for which $Ki \leq K\text{-}Si$ and $Ci \leq C\text{-}Si$

Typical elements of the first class are the alkalies, which have a leaching rate higher than that of silicon due to Na^+ and H^+ interdiffusion in the glass.

The second class comprises soluble elements that cannot diffuse in the glass; they are released to the groundwater when the SiO_2 matrix is dissolved. Technetium and neptunium in their higher oxidation states are typical of this type.

The last category comprises important elements such as plutonium and americium; due to their very low solubility they tend to be enriched on the glass surface layer and are released to the water body mainly as microcolloids.

Ultrafiltration experiments have been conducted [4] with leachates obtained from glasses spiked separately with americium, neptunium and plutonium. Figure 1 shows the percentage distribution of the various transuranics on different filter porosities. If the release of these nuclides was related only to the loss of the silica gel from the glass surface, all the elements would show the same retention pattern on different membrane porosities. It can be supposed that a hydrated layer of silica is formed on the surface of the glass, which becomes slowly enriched in lower solubility elements. The subsequent loss of this layer to the water vector, followed by the dissolution of the siliceous material, released the low soluble nuclides in colloidal form. The mean size of these colloids should therefore correlate with the concentration of the transuranic nuclide in the surface gel layer.

In the case of americium it has been found [5] that in a flowing system more than 90% of this element is released in colloidal form. The released activity reaches an equilibrium value, which may be due to the steady-state concentration of americium at the surface as well as the rate of disaggregation of the gel layer.

Differences in size distribution may also be interpreted by the formation of pseudo-colloids, between silica and the actinide, governed by the adsorption affinity of the various hydroxides.

3. FORMATION OF COLLOIDS BY REPRECIPITATION PROCESSES

The presence of radioactive colloids in groundwaters can be due not only to their direct release from the waste form but also to reprecipitation mechanisms of leached ions. These phenomena will be the consequence of the enhanced solubility in the thermal and radiation field around the waste. As the migrating species reach the temperature and redox conditions approaching the natural value, precipitation may occur giving rise to a solid phase. This phenomenon induces the formation of either real colloids or pseudo-colloids through the adhesion to naturally existing particulates in the interstitial water. The content of natural colloids in granite groundwaters has been measured in Sweden [6]. The concentration detected was less than 1 mg/L. It is presumed that if the natural colloid content remains at this low level even after the waste emplacement the transport by this route of radionuclides eventually released by the repository will be small.

Bacterial action is also believed to play a role in particulate transport. Remobilisation of ^{137}Cs in the CRNL aquifer [7] has been noticed to occur with particulate material in the size range of 0.2 to 1 µm. Cobalt-60 gamma irradiation showed that microorganisms are involved in the release or formation of particles associated with the transport of ^{137}Cs through laboratory soil columns.

In laboratory migration experiments with transuranic nuclides the redox conditions of the water vector have also been noticed to play a role [8]. Americium for instance becomes more mobile in anoxic conditions due probably to the fact that the iron present in the water is not precipitated as iron (III) hydroxide. In oxidizing environments, on the contrary, americium is sorbed on $Fe(OH)_3$ and is then retained on the geologic material by a filtration mechanism.

4. GENERAL CHARACTERISTICS OF COLLOIDAL OXIDES

The physico-chemical behaviour of colloidal hydrated oxides in contact with an aqueous solution is determined to a large extent by the dissociation of the hydroxyl groups. The following equilibria:

$$\text{M-OH}_2^+ \overset{H^+}{\rightleftarrows} \text{M-OH} \overset{OH^-}{\rightleftarrows} \text{M-O}^- + H_2O$$

$$\text{decreasing pH} \longleftrightarrow \text{increasing pH}$$

indicates that as a function of the pH the kinetic species may carry either positive or negative charges. At an intermediate value, the hydroxyl groups are undissociated and the surface reaches a point of zero charge (pzc). The pH at the "pzc" has a specific value for the various species, depending upon the electronic character of the metal-oxygen bond and the degree of stoichiometry of the surface.

Electrophoresis provides a useful tool for establishing the pH at which the particles do not move in an electric field. The "isoelectric point" (iep) is equal to the "pzc" when no specific adsorption occurs in the "Stern layer" [9,10].

Electrolytic adsorption may reverse the charge of particles and normally the "iep" shifts as the electrolytic concentration increases [11].

In the case of hydrophilic sols (as silica gel), a diffusive solvation shell may account for an extra stability factor of the colloidal suspension. The repulsion due to the ionized groups attached to the particle is responsible for an expansion factor of electric nature. This expanded structure is interpenetrated by a large volume of loosely bound water (solvation) which stabilizes the volume of the expanded particle.

In the presence of high concentration of electrolytes the "degree of solvation" of the colloid will be reduced. As a matter of fact, by adding an electrolyte, the diffusive double layer is compressed due to a weakened repulsion between the ionized groups; the swollen particle must expel part of the water until a new equilibrium between hydration and elastic forces is reached. In the case of a very high electrolytic concentration, such as in brine solutions, the solvation is also reduced due to a competition, in respect to the solvent water, between electrolyte and colloid.

5. MIGRATION IN THE GEOSPHERE

Evidence of the influence of colloids on the transport behaviour of radionuclides has been observed for both transuranics [4,12], as well as fission products [7,12]. Laboratory column experiments [4] studying the migration of transuranic nuclides leached from vitrified waste have shown that colloidal filtration is a major retention mechanism governing their transport through porous geological media.

A filtration model has been developed [13] making use of the experimental data of americium percolation through glauconitic sands. In Figure 2 the americium concentrations are reported for three columns corresponding to 28, 80 and 170 days loading experiments. The large percentage of americium retained on the filtering membrane (Figure 1) suggests that americium transport should be largely dominated by colloidal species. It is also evident from the smooth shape of the curve, that the colloid size is better described as a distribution rather than with a single value.

For a given filter coefficient λ the colloid migration can be described by the following set of equations:

$$\frac{\partial c}{\partial t} = - V \frac{\partial c}{\partial x} - \lambda V c$$

$$\frac{\partial \sigma}{\partial t} = \varepsilon \lambda V c$$

where $c(x,t)$ = moles of colloid in solution per liter of mobile water inside the column
$\sigma(x,t)$ = moles of colloid fixed by filtration per liter of column
V = interstitial velocity of the water (cm/s)
ε = kinematic porosity

For simplification we shall assume that, even if dispersion is not negligible, the advection process dominates. The solution of the filtration equations indicates that the profile of the retained colloids (σ) should be a straight line on a semilogarithmic diagram, the slope being proportional to λ. All the points in Figure 2 show, on the contrary, a profile strongly deviating from linearity.

This confirms the observation that the filtered colloids are distributed over a range of sizes. If the trend of cumulative distribution of sizes given in Figure 3 is assumed as being representative of the cumulative distribution of λ, a rough estimate of the distribution law can be obtained. A log-uniform or a log-normal distribution may be adequate to describe the observed trend. Naturally occurring phenomena often exhibit this latter distribution.

Figure 4 shows the total colloid concentration $C_T = \sigma + \epsilon C$ for the 170 days experiment. The line shown represents the theoretical profile calculated on the basis of a log-uniform distribution of λ, having extreme values of 0.2 and 10 cm^{-1}.

This very satisfactory fitting between the theoretical and experimental values is not reproduced for shorter percolation experiments. In the 28 and 80 days tests a plateau at 2.10^{-10} M* is noticed, which apparently shows contrasting features, i.e:

- it is established very rapidly (within 28 days)
- it does not increase with time

The most likely interpretation of this observation is that a sorption saturation mechanism is in operation. Concerning the low concentration level at which the saturation of the soil column occurs, we can assume that the species responsible for the sorption may be due to the smallest microcolloids or negatively charged species with affinity for a limited number of active sites on the column. For short percolation times the profile of the column is then described by a migration process with retention; after the saturation period of the column, the americium migrates as if there were no sorption, but only a filtration mechanism. As a matter of fact it has been found that a 5.10^{-13} M concentration of americium leaves the column very rapidly. It is clearly evident, moreover, that the plateau cannot be accounted for by the activity of the interstitial water, which is well below the observed saturation concentration.

An overall equation including both filtration of polydispersed species and sorption has been developed, which fits satisfactorily the three sets of experiments performed at different percolation times.

6. CONCLUSIONS

(1) The exact nature of the colloidal fraction released by the glass surface is not yet well understood; real colloids or aggregates between primary hydrolysis products of the radionuclides and hydrous polymer network of silicic acid may both be present.

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* M = mol/l

(2) Adsorption of radionuclides on microcolloids normally existing in groundwaters, or produced either by the corrosion of the container material or by degradation of the backfill, may be responsible for the transport as well as reprecipitation processes. The presence of a thermal gradient or of a redox front may enhance the importance of such mechanisms.

(3) The colloidal characteristics of the radionuclides released to the water vector depend upon the nature of the nuclide considered and the chemical environment. Adequate physico-chemical methods of characterization of the very diluted colloidal fraction have to be developed for a better description of the deep bed filtration processes.

(4) In laboratory column experiments, the following predominating processes have been identified:

   (a) colloid filtration: governed by a distribution of values of the filter coefficient (i.e. the colloidal fraction is polydispersed).

   (b) saturation phenomena: appears after a very short time and can be adequately described by a Langmuir isotherm.

   (c) escape of mobile species: after saturation a small fraction of the input activity flows through the column with practically no retention. It can not be ascertained at present whether this fraction is accounted for by the lower size microcolloids or by a soluble species.

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DISCUSSION

It was generally agreed that the direct release of colloids from the waste form is typical only of abnormal evolution of the repository, when flowing water contacts the waste. Reprecipitation phenomena on the contrary are possible at the interface between the "near" and "far field" as a consequence of the enhanced solubility in the thermal and radiation field. It has been suggested, however, that the dimensions and intensity of the "redox front" have to be considered site specific and design specific.

Concerning the division of leached radionuclides in three classes, it has been underlined that the tendency of the elements of the second class to form colloids, may be affected by subsequent redox reactions and/or interactions with barrier materials other than the glass waste form. For instance, in a case of a combination of spiked glass, basalt and container material, simultaneously in contact with synthetic basalt groundwater at 200°C and 30 MPa, the formation of particulate material composed of reduced species of technetium adsorbed on iron hydroxide has been observed.

In order to evaluate the dimensions, and possibly the distribution, of the colloids formed in the leaching of actinide loaded glasses, some recent measurements obtained with a Photon Correlation Particle Analyser were presented and discussed. The suspension examined was obtained using the same glass and conditions described by Avogadro; it has been confirmed that the suspension is polydispersed but the mean diameter of the colloids appears to be around 4 μm. Two types of glasses were examined and showed the same mean colloid diameter. Such a value is not in agreement with the ultrafiltration measurements if we assume that the radioactivity measurements shown in Figure 1 represent only real colloids formed by the actinide detected on the filter. However if it is assumed that americium is adsorbed on the surface of silica colloids, a good agreement is obtained considering a logarithmic (or log-normal) distribution of the silica colloids. Further tests are in progress with plutonium to confirm this hypothesis and to demonstrate the presence of real or pseudo-colloids in the glass leachate.

The need for an experimental distinction between real and adsorption colloids is not simply academic. The nature of colloidal particles affects the migration behaviour of radionuclides. Pseudo-colloids normally behave according to the chemical nature of the particulate matter the nuclides are adsorbed on. Real and pseudo-colloids show different sorptive properties, the former adsorbing more strongly on the soil material during the migration. Experiments on the migration of americium colloids through Al_2O_3 packed columns showed retention behaviour depending upon the pH of the solution. Studies on colloidal formation have been performed using ultracentrifugation, taking into account the effect of pH, radionuclide concentration and ionic strength. In the case of americium the formation of colloids becomes significant even at pH 3-4. Ageing also plays an important role on the aggregation, a large removal of americium from the solution being observed during the first 6 h.

The formation of clay colloids, and their radioactive transport capability, have been inferred to affect the choice of the backfilling material. In the case of glauconitic sand columns, reported in the previous discussion paper, no radioactivity associated with colloidal release from the columns was detected. This situation must be confirmed for other clay minerals foreseen as backfilling in the waste repository.

Concerning the effect of bacterial action on the reprecipitation and transport processes, it was argued that actinides released in ionic form could conceivably combine with $Fe(OH)_3$ formed by metal-oxidizing bacteria and deposited onto their cell walls. In addition, americium and cesium could be made soluble by combination with organic compounds and this will ultimately affect the radionuclide migration. It may be that gamma irradiation of soil, which is a procedure normally adopted for sterilizing laboratory columns, may have some effect on the radionuclide behaviour. Cobalt-60 irradiation will kill microorganisms, which may facilitate the movement, but the organisms themselves may not be the reason for the migration. Microorganisms do produce organic chelating agents that can solubilise metals.

As a final comment, it has been underlined that the filtration of colloids around the waste emplacement can be considered an effective retardation process in a short-term situation; but in the long-term situation the dissolution of these colloids may be the rate-determining step of actinide release toward the biosphere.

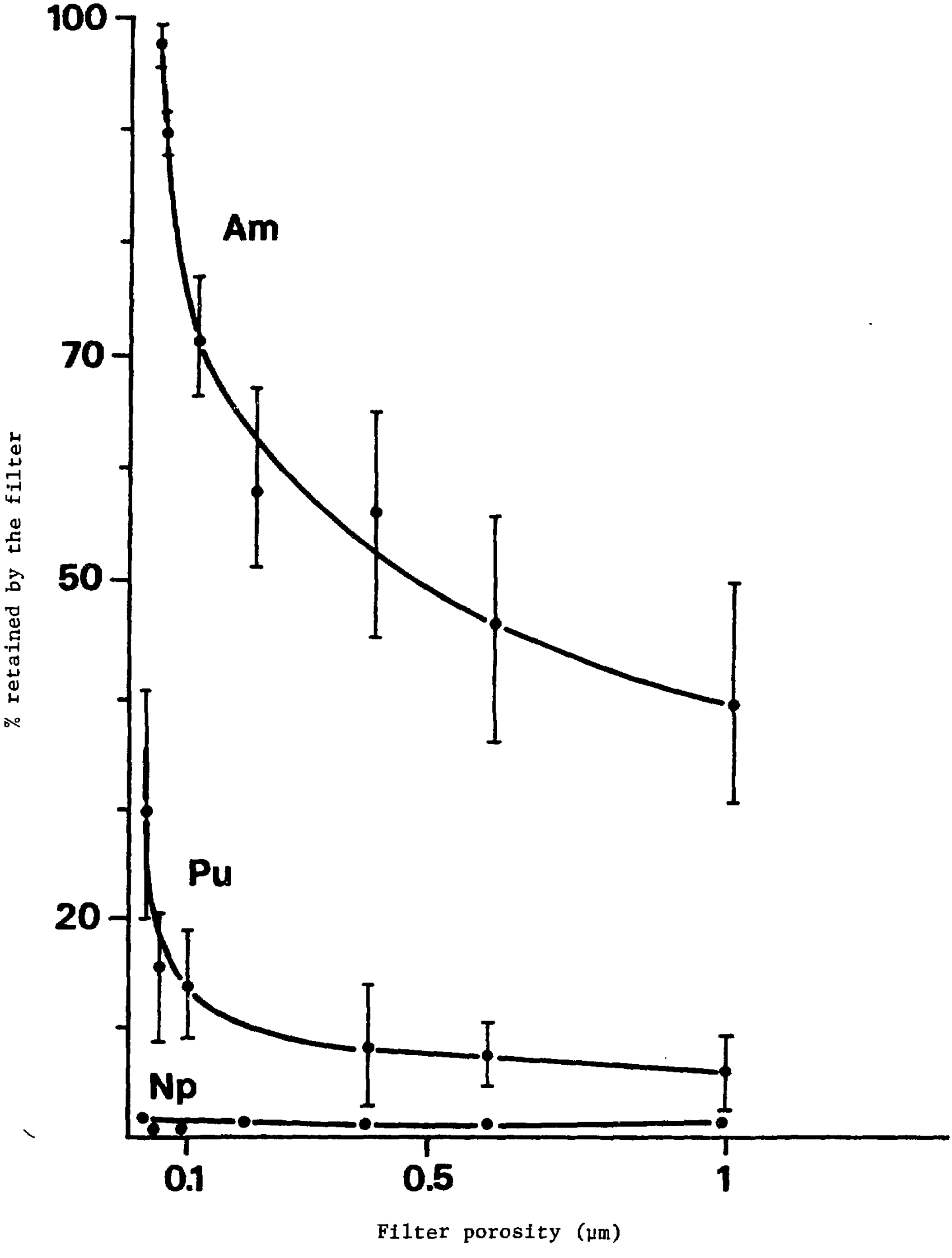

FIGURE 1: Percentage Retention of Leached Actinides Versus Filter Porosity (Nuclepore Membranes)

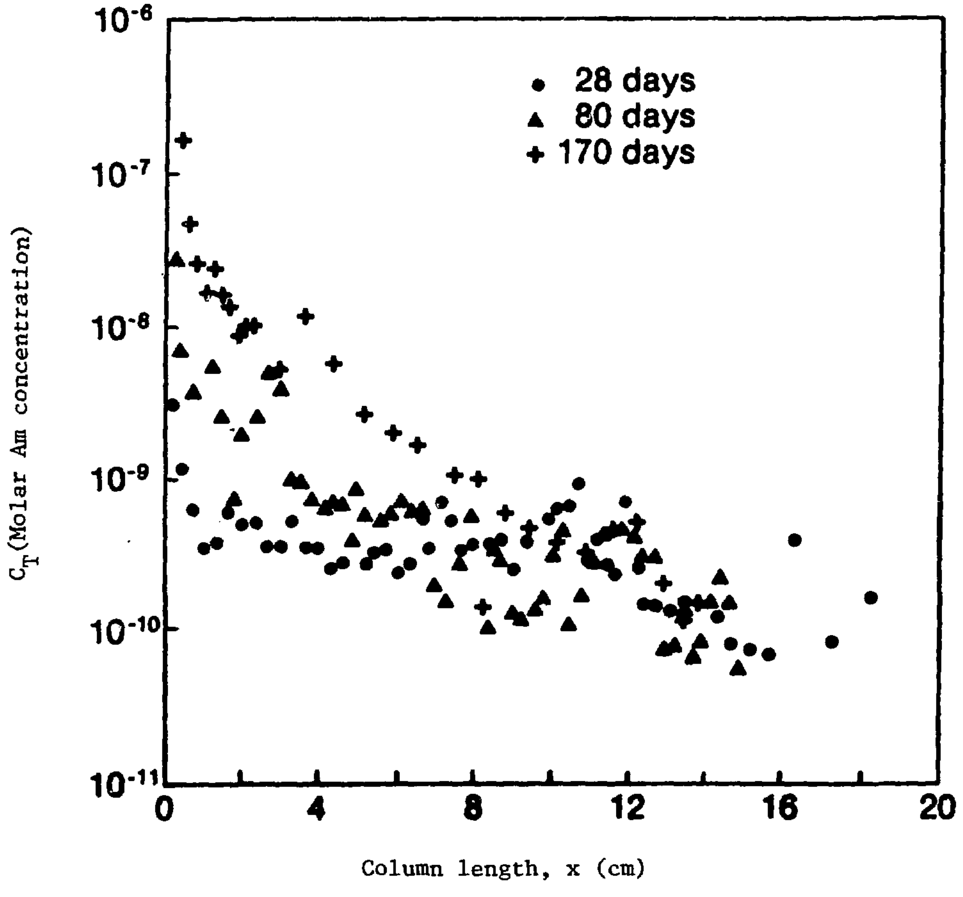

FIGURE 2: Americium Column Profile for Three Percolation Experiments of Different Length

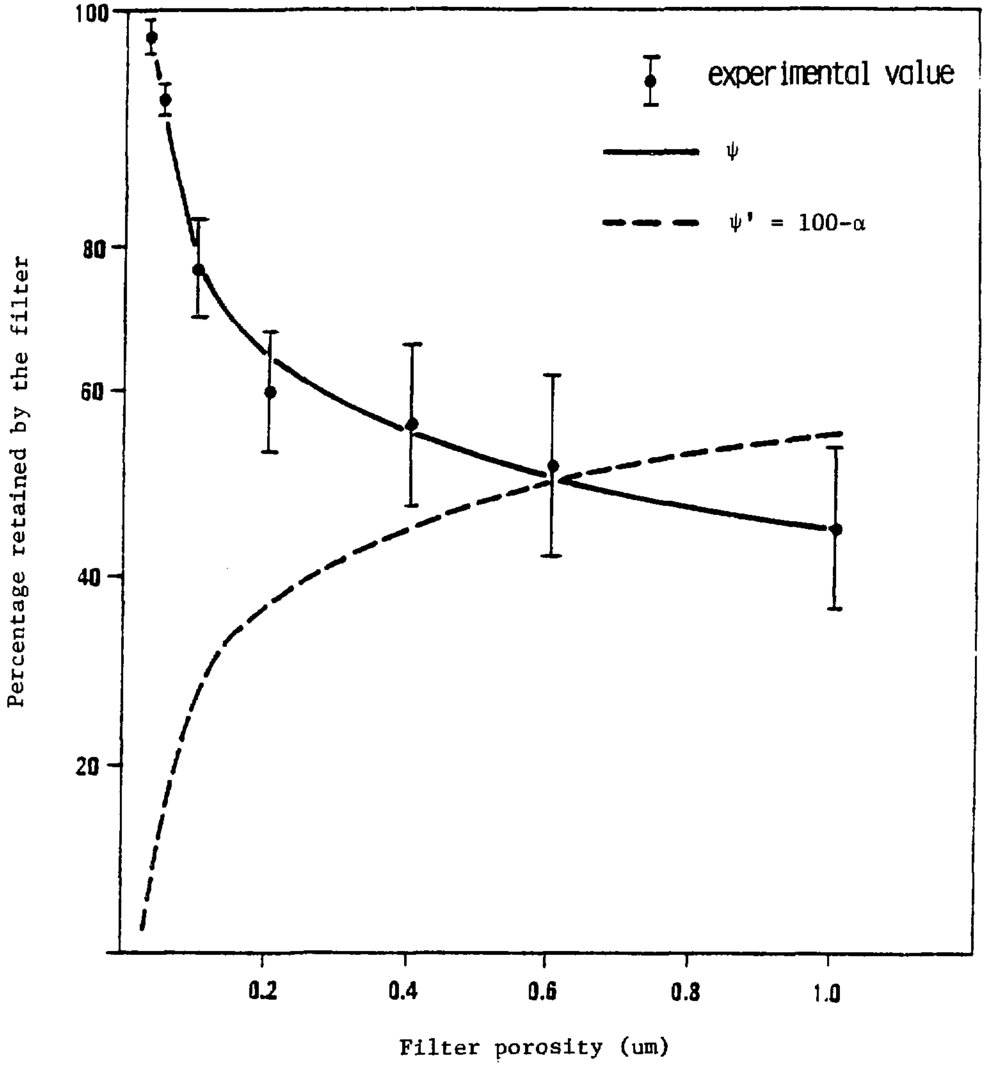

FIGURE 3: ψ = Retention of Leached Americium Versus Filter Porosity
ψ' = Cumulative Distribution of Sizes

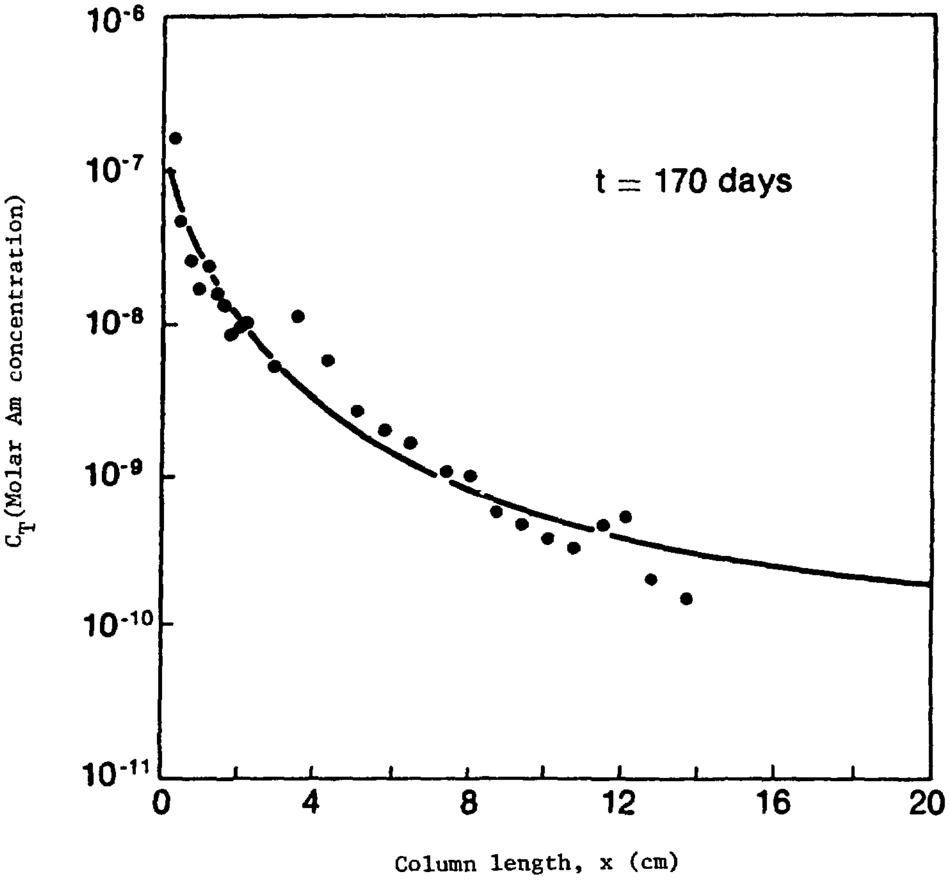

FIGURE 4: Americium Filtration Pattern, Comparison Between Experimental and Theoretical Data

TECHNIQUES FOR APPLYING COMPLEX SORPTION DATA FROM MECHANISTIC STUDIES TO TRANSPORT MODELS

Ian G. McKinley

1. INTRODUCTION

Almost all participants in this workshop will be perfectly familiar with the present status and limitations of existing radionuclide sorption programmes*, and although we could go over the familiar problem points of K_d versus isotherms, interpretation of Eh, etc., it would be more useful to consider the entire subject from the viewpoint of the mathematical modeller responsible for demonstrating the acceptability of a particular repository concept or site. We will thus consider the following scenario:

A repository location and design have been selected on the basis of geological/engineering criteria in a granitic rock body. All background geochemical and hydrogeological characterisation has been performed. Source-term and hydraulic flow models are available but the transport of nuclides from the waste canister to the surface must be modelled for the overall safety assessment. Within a defined time (5-10 years, say) such a model must be constructed and validated.

2. BREAKDOWN OF THE PROBLEM

(1) Define the components of the model on both micro- and macro-scales (almost any quantifiable process can be incorporated into present numerical models).

(2) Design the required experimental "sorption" programme with particular regard to methods for incorporating the data produced into the overall model.

(3) Specify techniques for model validation.

(4) Identify any problems that would inherently necessitate much longer term research programmes.

3. OVERVIEW

How would a programme constructed on the basis suggested above compare with existing programmes? In particular, are all the factors identified in (4) above being studied at present?

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* A perspective on this is appended at the end of this paper.

4. METHOD OF APPROACH - AN EXAMPLE

Based on the classification in the previous breakdown of the problem, one possible approach is described.

(1) On the simplest level consider two macro-compartments corresponding to the "near" and "far" field. The near field is obviously important as it defines the source input to the "undisturbed geosphere", but analysis of sorption processes within this region will be very complex due to perturbations of the natural system (varying in space and time) due to, for example, temperature and radiation fields, leachate chemistry and radiolysis products.

(i) Possible justification for ignoring the near field

For particular scenarios, nowever, it may be reasonable to ignore the presence of sorption in the near field (introducing extra "conservatism" into the overall analysis) depending on the extent of the near-field zone in comparison to the total flow path. In evaluating the extent of the near field, the most important process to be considered is probably the equilibration of the gross chemistry of the leachate (including radiolysis products) with the rock phase in which both thermodynamic and kinetic factors may be important. In consideration of either of the macro-compartments in detail, the next requirement is:

(ii) Physical description of groundwater flow

In the reference scenario, fissure flow is specified but, on a micro-scale, this could occur as "laminar" flow through open fissures (whose surfaces may be covered by a layer of hydrothermal alteration products) or as "porous" flow through relatively permeable infill material. Diffusion of solutes from the fissure into "dead-end" pores or the non-flowing porosity of the rock matrix must be considered along with the nature of the rock surfaces in contact with such diffusing solute.

(iii) Mechanisms of solute retardation

Such mechanisms can be broadly classified as either dependent on, or independent of, the rock phase composition although, in real life, the boundary between these classes may be rather indistinct (e.g. processes thermodynamically independent of solid phase may be kinetically controlled (catalysed) by particular surfaces). Rock phase independent retardation - precipitation/dissolution processes - is primarily dependent on the bulk chemical composition of the aqueous phase.

All other solid phase dependent retardation processes can be regarded as "sorption" and include physical sorption, ion-exchange, surface mineralisation etc. Ideally, all uptake processes would be studied independently but, as a minimum requirement, the variation of overall "sorption" with a number of environmental parameters must be quantified. Important variables that must be considered include

(a) reaction direction (sorption/desorption)
(b) nuclide concentration
(c) gross groundwater chemistry (Eh, pH, major ions)
(d) mineralogy (if variations occur along the flow path)
(e) particular trace species (due to the effects of competition, complexation, etc.)

(iv) Possible complicating factors

Finally, the possibility of processes occurring that could cause deviations from the assumed simple homogeneous geochemical system must be considered. Possible candidates include colloidal transport (both on naturally occurring colloids and those formed as a consequence of near-field processes), the existence of very sharp redox boundaries (which may arise if radiolysis causes an oxidising near field) and microbial effects.

(2) Particular experimental approaches that might be applied to study the four problem areas highlighted above include

(a) Integral waste-leaching/migration experiments to study near-field processes.

(b) "Column" migration experiments to examine the physical details of groundwater transport of nuclides.

(c) "Batch" sorption experiments to examine the mechanisms of particular uptake processes.

These different types of experiment produce different types of data, which must all be incorporated into overall assessment models. Methodology (a), and scoping experiments to examine the influence of additional processes (e.g. colloids, microbes) using variations of techniques (b) and (c) are likely to produce data that are semi-quantitative at best and are primarily aimed at justifying model simplification by ignoring particular processes. Column experiments (b) may produce mechanistic information on flow processes (especially when combined with autoradiography) and quantitative measurement of overall retardation. Batch sorption measurements (c) form the essential background to any retardation study and should provide the quantitative mechanistic information required to allow data extrapolation over the geological timescales involved.

(3) Techniques for validation primarily involve in-situ migration experiments and natural analogue studies. In both cases experimental data and associated models should be used to predict migration prior to its experimental measurement. While this requirement might seem obvious,

many studies to date have involved use of models to explain previous measurements of migration. Such work tends to involve interesting exercises in curve fitting but can, in no way, be regarded as model validation.

(4) Particular problem areas, which require long-term research programmes, include both long timescale experiments (e.g. in situ migration or integral leaching/migration) and areas of critical importance in which very little progress is evident at present. In the latter category, the extraction of mechanistic information from batch sorption data might be mentioned in view of the slow current rate of development of both experimental design and data interpretation.

RADIONUCLIDE SORPTION MEASUREMENTS IN PERSPECTIVE

1. INTRODUCTION

A major argument in favour of geological disposal of nuclear waste is the fact that the rock body itself acts as a final barrier to the release of radionuclides in the event of all other "engineered" barriers failing. It is generally acknowledged that by far the most likely cause of radionuclide release from the near-field is groundwater ingress despite the very long timescale required for degradation of backfill, overpack, canister and waste matrix. In the evaluation of any potential repository site, therefore, an important parameter is the extent to which nuclides may be retarded during groundwater transport due to sorption onto the host rock.

In this context, the general term "sorption" is used to cover all physical and chemical processes that transfer dissolved species from the aqueous to the rock phase (including, for example, physical adsorption, ion-exchange, mineralisation, etc.).

Until relatively recently the role of the scientist measuring sorption was simple: transforming an analogue input (rocks from field geologists) into quantitative numerical data (K_d's) which could then be handed to the pure mathematicians and computer scientists to be placed in context via their models (Figure 1). Advances in both experimental technique and data interpretation have resulted in sorption information which, although possibly stated with more caveats than in the past, reflects a deeper understanding of the mechanistic processes occurring and the limitations of particular experimental techniques. With the realization of the great complexity of "sorption" processes in the real environment it is thus essential that experiment design and data output should be viewed in the perspective of particular, site-specific applications.

2. GEOLOGICAL CONTEXT

Sorption studies generally fall into one of three broad classifications:

(a) Site- and application-specific empirical research
(b) "Academic" study of sorption processes on simple substrates
(c) Investigation of natural analogues.

While the first of these categories forms the major part of nuclear waste related research in this field, it is important to realize that (b) and (c) are essential components of the transformation of sorption data to model parameters as, only when backed by information from either (or preferably both) of these sources, can the extrapolation from laboratory to repository timescales be justified. Thus, even for work of indirect application, it is important that the final context of data use be considered. For example, if water flow occurs through clay infilled fissures, basic sorption research might be better focussed on individual clay minerals than minerals derived from the bulk rock matrix. Similarly, a natural analogue study of migration through a very porous medium may have very little relevance to environments in which fissure flow dominates.

For category (a) above, however, specification of context for the measurements is especially crucial. A measurement of sorption of a nuclide from distilled water onto an undefined lump of rock cannot even be regarded as an order of magnitude estimate of retardation - it is a totally meaningless datum outside of the simple laboratory context. Selection of rock samples is obviously of great importance - to a chemist a glacial erratic lying on the surface might look as good as any other rock but its relevance to deeper formations may well be negligible. Sample selection is not, however, simply the province of the hard-rock geologist as, for meaningful sorption data, hydrogeology must be considered on both a macro - (formations in which regional flow occurs) and micro-scale (determination of the actual rocks in contact with migration nuclides). Determination of groundwater chemistry and estimating its natural spatial variability and evolution over the timescale considered is an art in itself but is further complicated by the possible perturbations due to repository emplacement. For sensible experiment design the source term into the formation considered must also be estimated along with its own spatial and temporal variability (especially complex in the case where different nuclide species can compete for sorption sites).

Various representations of the "geological context" are shown diagramatically in Figure 2.

3. EXPERIMENTAL METHODOLOGY

In principle, the measurement of radionuclide sorption is very simple. In the most common batch equilibration technique a sample of rock is incubated with radionuclide-spiked groundwater and the resultant concentrations in both the solid and liquid phases measured (Figure 3a). Alternatively, spiked solution is passed through a column of rock material and sorption is evaluated indirectly by comparison of the input profile (generally a pulse or step function) with the observed concentration profile either as a function of distance along the column or of time in the output solution (Figure 3b). On a field scale, spiked solution can be pumped between boreholes and retardation calculated from comparison of the breakthrough curve with that of an "unretarded" tracer (Figure 3c). Naturally, in real life, design of such experiments is a much more subtle process than implied above but many protocols exist to provide reproducible data from any particular type of experiment.

As shown in the illustrations, the results of each of these experimental approaches are generally presented as "K_d" values but it must be emphasized that these data do not necessarily correspond to the same physical measurement. This fact is apparent from inspection of Figure 3, i.e. 3a measures the ratio of activities directly on an isolated rock sample, 3b measures retardation during flow through a well-defined sample, while 3c measures retardation through an effectively unknown substrate. In order to derive a "K_d" from 3b or 3c, assumptions must be made about the actual processes occurring - generally all retardation is taken to occur by reversible, concentration-independent sorption. Despite the widespread use of such assumptions, batch experiments of type 3a often show sorption to be at least partially irreversible with strong concentration dependence. It must also be emphasized that "sorption" is only one of a number of processes that might cause the retardation observed by 3b and 3c experiments, others likely to be important in particular cases being dissolution/precipitation reactions and physical retardation (e.g. diffusion into dead-end pores in the rock matrix). The sum of these processes appear as a "retardation factor" but individual contributions must be separated out for modelling purposes.

Even when sorption data for a well-specified system are reported, it is essential to stress the limitations of resulting numerical values - not in terms of simple counting statistics (which can be made as small as desired) but by analysis of replicate samples that reflect inherent variability (generally due to the heterogeneity of natural materials). Limitations in direct applicability (e.g. single nuclide spike sorption data) must be very clearly stated or, if possible, demonstrated by use of simple, process-oriented models.

The form of data output is dependent on the end user but there should always be a positive feedback to allow improvement of methodology and possible constraint of the values of poorly defined environmental variables. For most real systems individual data points are of little use and hence data presentation should always emphasize observed trends in empirical data sets and, where possible, suggest methods in which such trends could be tested against observations in analogue systems or more basic mechanistic studies.

4. CONCLUSIONS

Within the waste management context, the entire "raison d'etre" of sorption studies is to provide data for safety assessment models (a fact that might not be apparent from perusal of the sorption literature). While there is some evidence that design of experimental methodology is developing in order to produce more relevant data, the essential two-way link between experimentalists and mathematical modellers is still weak.

It has been noted that experimental measurements of sorption are generally actually measurements of nuclide loss from solution or retardation in a particular transport set-up. Translation of measured parameters into sorption data is based on implicit mechanistic assumptions. These should be continually rechecked by as many independent methods as possible. For example, all experimental techniques contain the implicit assumption that microbiological effects are insignificant yet microbial contamination, to some extent, will certainly occur.

In most cases such assumptions would probably be valid but their explicit statement serves as a reminder of potential limitations of mechanistic interpretations and may suggest development of technique to allow quantification of their possible effects.

Measurement of sorption data is an integral part of the safety assessment for nuclear waste disposal and requires background input from all other components of such a programme, ranging from field measurements to modelled release scenarios. The requirement exists for those using sorption data to understand more about their origin and limitations but, equally, anyone measuring sorption parameters must be aware of the context in which this work is placed.

DISCUSSION

The session was introduced by emphasising the importance of viewing sorption experiments and data in a nuclear fuel waste disposal context. Sorption in this context was defined as any process retarding the migration of dissolved species.

Several contentious proposals were then advanced for discussion:

(1) Most sorption data more than $\sim$ 5 years old and measurements on pristine rock (as opposed to hydrothermal fracture infillings) are probably completely irrelevant to nuclear waste disposal studies.

(2) The systems involved are probably well enough understood for "matrix-type" batch sorption experiments (involving thousands of individual samples) to be designed, which would produce empirical functions describing sorption as a function of Eh, pH, temperature, concentration, aqueous chemistry, reaction direction etc. Such functions could be prepared in a relatively short time ($\sim$5 years) and be incorporated into numerical flow models, which would then probably be sufficiently good for the entire sorption problem to be regarded as "solved".

(3) With the range of expertise available at the meeting, the research programme required to perform this research, validate it and identify any long-term problems can be described.

The main points to arise from the occasionally heated discussion of these proposals were

(1) Complete disregard of all "K_d" sorption data is unrealistic in that, as long as experimental conditions were reported in detail, such basic information can be used to examine predicted trends from mechanistic studies.

(2) Considerable polarisation of views on the second proposal was evident. For the application of empirical data to safety models it was noted that justification of the extrapolation of such data beyond laboratory timescales was only possible by use of mechanistic, thermodynamic or

natural analogue data, or preferably all three. It was noted that a progression from "matrix-type" batch sorption methods, column/rock transfer methodologies, integral leach/migration studies, small scale field experiments, short term analogue, (e.g. chemical waste) and long term analogues (natural disequilibria) was evident where the advantages of increasing timescale and realism must be set against decreasing accuracy of knowledge of system parameters (e.g. flow, reaction time etc). Most criticism of the proposal centred on the lack of emphasis on mechanistic or thermodynamic data. In particular, the crucial importance of the kinetics of surface reactions was noted as it was pointed out that slow reactions which may be difficult to observe in a batch experiment, especially if irreversible, would dominate over other sorption processes in the nuclear waste context.

(3) The proposal to design a full experimental programme (as described in the original discussion document) was not fully discussed but a general concensus for the following was evident:

  (a) The entire existing set of "good" sorption data should be reviewed in the context of expected repository flow conditions, radionuclide inventories, and toxicities and with consideration of geochemical observations and existing thermodynamic data, to define the sorption problems existing and those effectively solved.

  (b) Analogue studies to determine the applicability of extrapolation of sorption data to longer timescales, in at least an order of magnitude basis, are urgently required.

  (c) Longer timescale studies to examine mechanisms have been noted and in such studies surface chemistry should play a more prominant part. Such studies can probably only be defined in detail after (a) and (b) above. With the general definition of "sorption" used, microbiology could be important but as yet, no real data exist on this topic; however, but background scoping research is required.

The following conclusions were reached:

(1) Existing sorption programmes are poorly coordinated scientifically and a review of existing data should be conducted specifically to identify research areas that are effectively solved (and need no longer be funded) and the few problem areas that exist - probably mainly regarding possible retardation of Tc, I (for disposal of fuel), Ra, Np and U and sorption of problem nuclides in the near field.

(2) Analogue studies are required over a range of time-scales and, in particular, regions where migration has occurred through granite fissures.

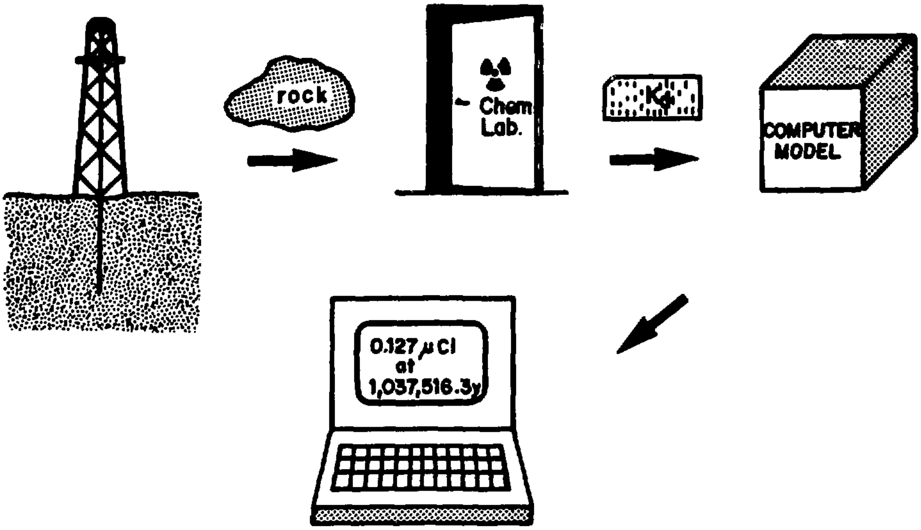

FIGURE 1: Schematic Representation of How Data is Collected from Field and Laboratory Research and Incorporated Into Computer Models

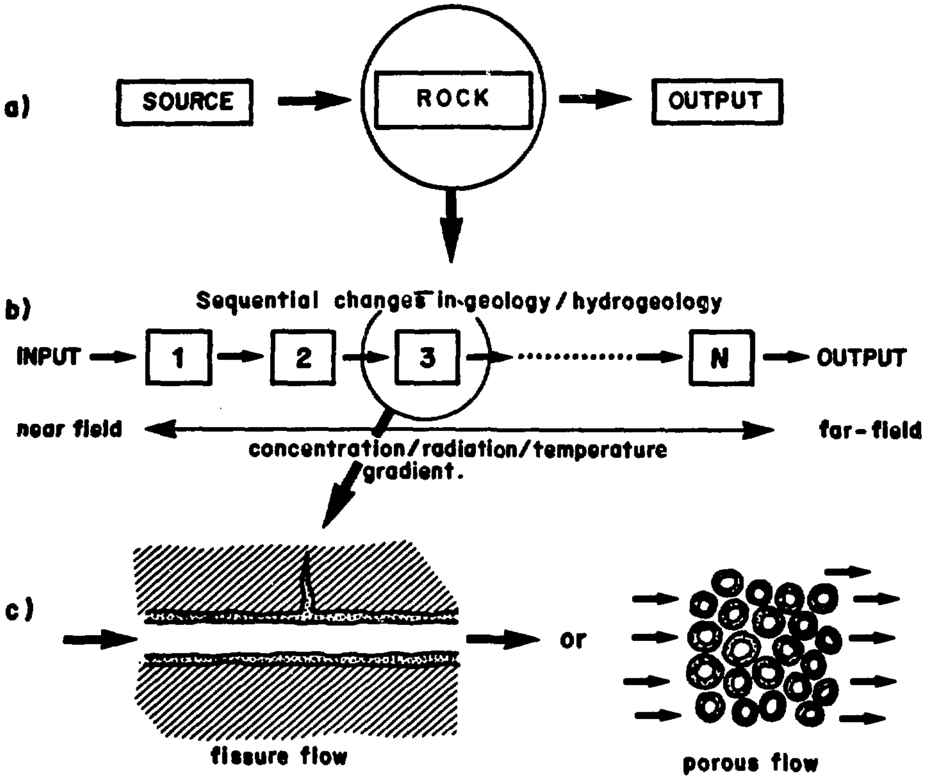

FIGURE 2: Various Representations of the "Geological Context"

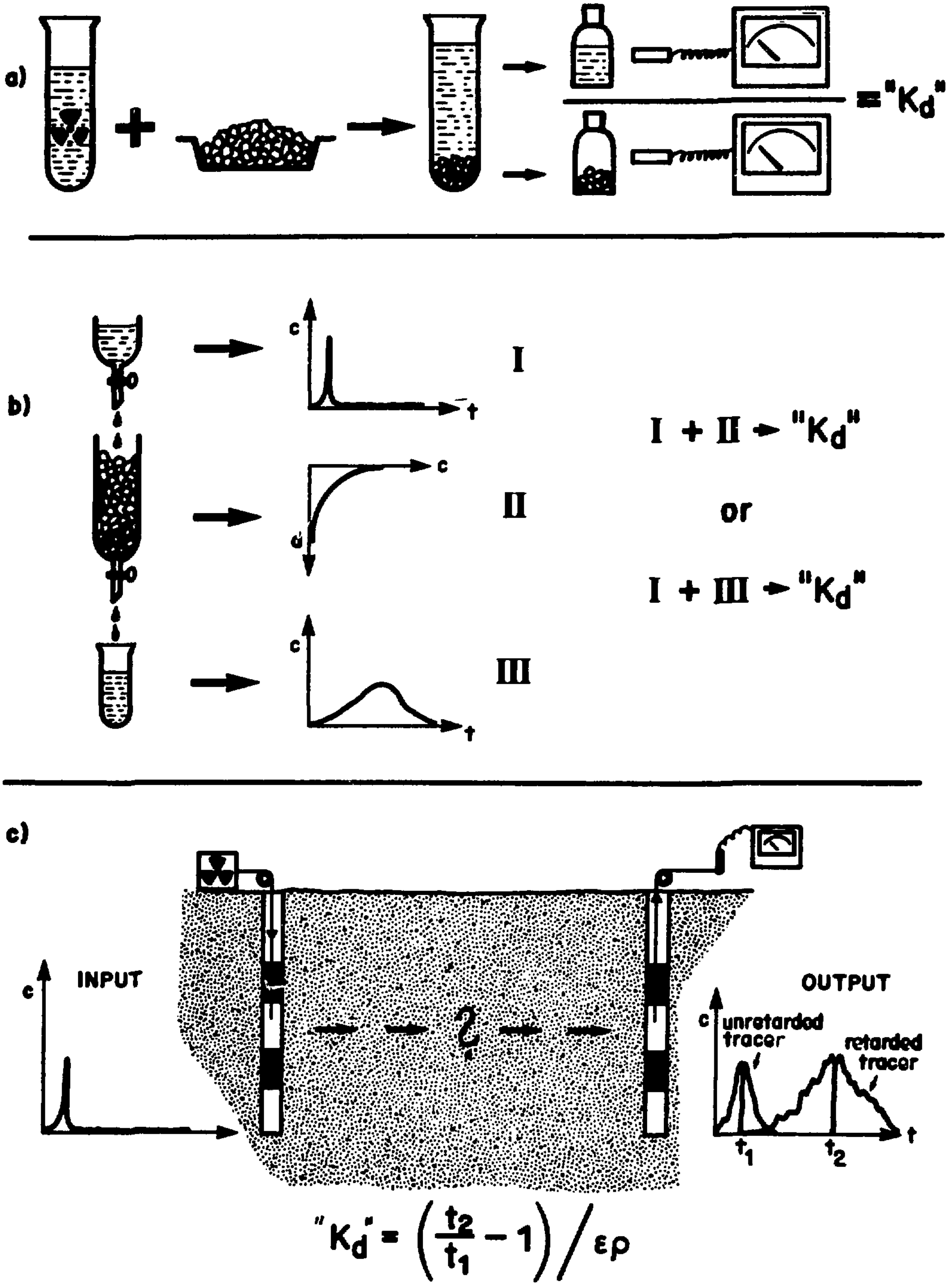

FIGURE 3: Schematic Representations of Ways K_d and Retardation Factors are Determined Experimentally in the Laboratory and in the Field

LINKING FLOW AND GEOCHEMICAL MODELS: STATUS AND PROBLEMS OF DEVELOPING A FULLY COUPLED MODEL

F.J. Pearson, Jr.

1. INTRODUCTION

To model the chemical behaviour of flowing groundwater requires consideration of two processes - water flow and geochemical reactions.

Water flow is described by the continuity equation and its supporting relationship, Darcy's law (written in one-dimension for simplicity):

$$v = - \frac{\kappa}{\mu} \left(\frac{\partial p}{\partial x} + \rho g \frac{\partial h}{\partial x}\right) \qquad (1)$$

where: v = specific discharge (Darcy flux) ($m^3/(m^2.s)$);
κ = intrinsic permeability of the medium (m^2);
ρ = fluid density (kg/m^3);
g = gravitational acceleration constant (m/s^2);
μ = dynamic viscosity ($kg/(m.s)$ = Pa.s);
p = fluid pressure ($kg/(m.s^2)$ = Pa);
h = hydraulic head (m); and
x, the flow direction, is not necessarily horizontal.

The form of Darcy's law used for most laboratory and simple, shallow field problems is

$$v = - K \frac{\Delta h}{\Delta x} \qquad (1a)$$

where K is the hydraulic conductivity ($m^3/(m^2.s)$) and equals $\kappa\rho g/\mu$.

The chemical part of the problem is described by conservation of mass equations, which can be written in terms of the solution concentrations of species of interest:

$$\frac{\partial(\phi C_i)}{\partial t} + \frac{\partial}{\partial x} \left\{ C_i v - \phi D \frac{\partial C_i}{\partial x} \right\} = \Sigma R \qquad (2)$$

where C_i = concentration of dissolved species i (kg/m^3 fluid);
ϕ = porosity of the medium (m^3 fluid/m^3 matrix);
D = coefficient of hydrodynamic dispersion (m^2/s); and
ΣR = net rate of production (or consumption) of species i ($kg/(m^3/s)$).

In equation (2) the first expression represents the rate of change of mass of the species in solution in a volume element. The second expression represents the net mass flux of the species into and out of the volume by convection (the first term in brackets) and dispersion (the second term in brackets). The R terms represent all sources and sinks of the species including reactions between the fluid and the matrix and, for radioactive waste problems, species decay or production, waste-form leaching, and so on.

1.1 SOLUTE TRANSPORT MODELS

Most approaches to the problem to date can be called solute transport models. They do not represent a true coupling of chemical reactions with flow, because they include various assumptions that limit their generality. A common assumption is that fluid flow is entirely independent of chemistry. This is mathematically equivalent to saying that the fluid flux term (v) in equation (2) does not depend on any changes that may occur in C_i.

Additional assumptions are made in structuring the R terms. Certain transport models, for example, are written to simulate only the effects of dispersion and convection on solute concentrations (Konikow and Bredehoeft, 1978). The R terms in them represent only external sources or sinks of the solutes.

The R terms describing chemical reactions included in many solute transport models have been chosen less for their chemical accuracy than to permit structuring the resulting transport equation in a form for which a closed mathematical solution can be found. Furthermore, both to generate simply solved expressions, and because of a lack of data on reaction kinetics, it is commonly assumed that reactions are equilibrium controlled. That is, it is assumed that the rate of change of the concentration of a species as a result of chemical reactions is so much faster than its rate of change due to convection and dispersion that all chemical reactions can be treated as if they were at thermodynamic equilibrium at all times.

The R term in most equilibrium-controlled solute transport models expresses the concentration in the fluid as a function of the composition of the solid in the volume element. Under these conditions, the solute transport equation can be written:

$$\frac{\partial}{\partial t}(\phi C_i + \rho_b \bar{C}_i) + \frac{\partial}{\partial x}\left\{C_i v - \phi D \frac{\partial C_i}{\partial x}\right\} = 0 \qquad (3)$$

where $\bar{C}_i$ = concentration of constituent i in solid phase (kg/kg matrix); and
ρ_b = bulk density (kg/m^3).

The relationship between C_i and $\bar{C}_i$ is commonly described by a simple expression called an isotherm, by analogy with the forms of equations used to describe gas sorption data. A number of isotherms have been proposed particularly in the soils literature where they have been used to simulate a variety of types of column study results (van Genuchten and Clearly, 1979).

The simplest isotherm and the one most widely used in radionuclide transport modeling is the linear isotherm:

$$k_d = \bar{C}_i / C_i \tag{4}$$

where k_d = distribution coefficient of i (m^3/kg).

This isotherm can be interpreted as describing a simple sorption process or ion exchange when the species being modeled is present only in trace amounts.

To account for radioactive decay (or any other first-order production or consumption reactions in the system) additional R terms must be included of the form:

$$\lambda(\phi C_i + \rho_b \bar{C}_i) \tag{5}$$

where λ = radioactive decay constant for i (s^{-1}); and
$(\phi C_i + \rho_b \bar{C}_i)$ = total mass of i in volume element.

From these expressions an equation for the equilibrium-controlled transport of a trace radionuclide emerges:

$$\begin{aligned} &\frac{\partial}{\partial t}\, \phi C_i\left(1 + \frac{\rho_b k_d}{\phi}\right) + \frac{\partial}{\partial x}\left\{C_i\, v - \phi D \frac{\partial C_i}{\partial x}\right\} \\ &\qquad + \lambda \phi C_i\left(1 + \frac{\rho_b k_d}{\phi}\right) = 0 \end{aligned} \tag{6}$$

The expression in parentheses in equation (6) is the retardation coefficient (R_d), which is the ratio of the transport velocity of i to the velocity of an ideal tracer in the system.

Solute transport in the natural environment occurs in systems of complex geometry with spatially varying properties and often with fluid flow or solute input rates which vary with time. Thus, in practice the solute transport equation must be evaluated using numerical techniques that involve spatial and temporal discretization of the problem. The sizes of the discrete steps and the algorithms for averaging over them in space and time must be carefully chosen to minimize or eliminate errors in the solution due to numerical dispersion or truncation. Criteria for selecting block sizes and time steps for a given problem are known. They are based on the relative importance of convective to dispersive transport and for rate-controlled reactions such as radioactive decay on the relationship between transport and reaction rates. An acceptable solution to a large-scale field problem may require many blocks and time steps and be limited by the availability of computer resources. Thus, the new generation of transport codes is being designed to take advantage of the array processing capability of the newest scientific computers.

1.2 TRANSPORT IN FRACTURED MEDIA

In a fractured medium, fluid moving through connected fractures is in contact with more slowly moving or stagnant fluid in dead-end fractures or intervening porous media. It has been found that to simulate transport in such a system requires a model that considers transport in the connected fractures separately from that in the remainder of the matrix. In these dual porosity models it is assumed that convective transport occurs in the fractures and that there is much slower exchange with the (relatively) immobile fluid in the material between the fractures. Descriptions of a number of models of this type have been given recently, of which the numerical approaches taken by Grisak and Pickens (1980), Bibby (1981) and Huyakorn et al. (1983) can be mentioned.

In spite of the assumptions limiting the generality of the solute transport equation (6) and its extension to dual porosity media, they have been successfully used to simulate the transport observed in a number of laboratory and field problems. Laboratory or column studies commonly make use of closed form solutions, while for field studies, numerical solutions are more often used.

1.3 SUMMARY

Before proceeding with the discussion of approaches to constructing general geochemical-fluid flow models, it is useful to reiterate the assumptions common to most solute transport models:

- The only chemistry included is:
  - radionuclide (first-order) production or decay; and (or)
  - sorption or idealized exchange reactions;
- Only equilibrium-controlled chemical reactions are considered; and
- Fluid flow is not dependent on chemical changes in the system.

The remainder of this discussion will focus on what has already been done or needs still to be done to lift these restrictive assumptions.

2. EQUILIBRIUM CHEMICAL REACTIONS

The theory and practice of modeling equilibrium geochemical reactions is well advanced and, as a number of recent reviews of the technology are available (Nordstrom et al., 1979; Mercer et al., 1982; INTERA, 1983b), only the briefest summary is appropriate here.

Equilibrium geochemical models comprise

- An aqueous model, which computes the thermodynamic activities of dissolved species from their mass concentrations; and

- A reaction model, which calculates the masses of constituents transferred among phases to bring the system to equilibrium.

Two types of reaction models are available. Mass transfer models solve directly for the masses of constituents that exchange among phases to reach equilibrium from an initial state. PHREEQE (Parkhurst et al., 1980; INTERA, 1983a) is a well-known mass transfer code, and like others of its type, solves the equilibrium problem quickly and efficiently.

The second type of reaction model does not solve directly for complete equilibrium in a system, but calculates the incremental mass transfer that takes place during the course of a reaction. Such reaction path codes, exemplified by EQ3/EQ6 (Wolery, 1979, INTERA, 1983b), require greater computer resources than mass transfer codes, but provide in return greater flexibility in simulating chemical changes, including the ability to vary the relative rates of reactions.

Geochemical models by themselves have been used to simulate the spatial changes in rock and water chemistry that are observed in groundwater systems and ore deposits (Plummer et al., 1983). These spatial changes result from increasing reaction progress with fluid flow, and thus their simulation is, implicitly at least, a coupling of geochemical reaction modeling to flow. Papers by Thorstenson et al. (1979) and by Kwong et al. (1982) are recent examples of this approach to a regional aquifer system and to an ore deposit, respectively. While neglecting dispersive transport, as this approach does, may produce acceptable results in regional systems, smaller scale problems cannot be satisfactorily simulated without including dispersion (Routson and Serne, 1972).

2.1 DIRECT COUPLING APPROACH

Two approaches are taken to improve the representation of chemical reactions during transport. These can be termed the directly coupled and the iteratively coupled approaches. In the directly coupled approach, transport equations similar to (3) are written for each species i to be modeled. The relationship between dissolved and solid concentrations (C_i and $\bar{C}_i$) of individual species and among the several species themselves is described by conventional chemical mass action and mass balance equations. The chemical and transport equations are algebraically manipulated into a single set of new equations, which tend to be highly non-linear and so require relatively sophisticated numerical techniques for their solution.

An early directly coupled model is that of Rubin and James (1973), which describes the transport of two exchanging constituents i and j. The transport equations for these constituents are coupled by a mass action equation:

$$K_{ij} = \left(\frac{\bar{C}_i}{C_i}\right)^a \left(\frac{C_j}{\bar{C}_j}\right)^b , \qquad (7)$$

where K_{ij} = selectivity coefficient; and

a and b = valences of j and i, respectively, and by the constraint that the total exchange capacity of the substrate $(\bar{C}_T)$ is constant: $\bar{C}_j + \bar{C}_i = \bar{C}_T$.

More recently, Valocchi, Street and Roberts (1981) described a similar model, which has been extended to three exchanging solutes. They showed the results of its use to simulate changes in groundwater chemistry resulting from the injection of treated municipal effluent into a shallow alluvial aquifer.

The Rubin and James, and Valocchi, Street and Roberts models are considerable improvements on the conventional solute transport models in that they both consider the transport of several reacting components. Neither of them is particularly sophisticated chemically because their mass action expressions are written in terms of concentrations rather than as thermodynamic activities and neither includes such intra-solution behaviour as complex ion formation nor considers the formation or dissolution of solid phases.

A thermodynamically more rigorous, directly coupled model has been described by Miller and Benson (1983). While the only solid-fluid reaction included is ion exchange, solution complexing reactions are included and thermodynamic activities, rather than concentrations are used in the mass action expressions. The model was used to simulate the injection test data given by Valocchi et al. with excellent results.

2.2 ITERATIVE COUPLING APPROACH

The second approach to improving the representation of chemical reactions during transport is the iteratively coupled approach. This takes advantage of the large body of experience developed simulating the transport of non-reacting or simply reacting solutes and of the availability of the theoretically sound and efficiently coded chemical reaction models mentioned above. Basically, this approach begins with a flow model for non-reacting solutes to transport constituents through the system. After each time step of transport a geochemical model is called and the material in each block is allowed to react to equilibrium before taking the next time step of transport.

Grove and Wood (1979) defined such a model, which they used to describe the chemical changes during an artifical recharge experiment. They considered mineral dissolution-precipitation reactions, the formation of solution complex ions in solution, and cation exchange. The transport considered is one-dimensional and includes longitudinal dispersion. A finite difference method centered in space and time was used for its solution. Figure 1 of the report by Grove and Wood is a flow diagram for their transport-reaction program and clearly illustrates the operation of such an iteratively coupled chemical and flow model. Grove and Wood did not make use of an existing geochemical reaction model but constructed their own reaction routine for their specific problem.

More recently, Walsh et al. (1982) described a more complex iteratively coupled model. Their intent was to simulate the chemical changes accompanying sandstone acidization with HF/HCl mixtures and to examine the permeability reduction that often occurs at the start of such treatment. Their chemical model, which makes use of at least key parts of the geochemical code MINEQL (Morel and Morgan, 1972), includes seven elements, 30 aqueous species and a possible 14 minerals. A simple one-dimensional flow model was used, which was evaluated using an explicit backward-in-space, finite difference technique. The numerical dispersion introduced by this solution technique was used to account for physical dispersion.

Although the aim of the work was to simulate permeability changes, the effects of the chemical changes were not included in their chemical-flow model. Instead, following the simulation, porosity changes were calculated from the specific volumes of minerals dissolved or precipitated in each block. These in turn were used to calculate new permeability values using an empirical equation. In spite of its shortcomings, this approach is the most ambitious coupling of flow and chemical models yet undertaken and illustrates the power of the iterative coupling approach.

Iteratively coupled models will be required for most field studies because of their inclusion of relatively general chemical routines and their ability to calculate transport in complex flow systems. These models will require complex numerical methods for their solution and, before they can be widely applied, will require verification. The directly coupled codes are generally limited to systems of relatively simple flow and chemistry. However, their relatively straightforward mathematical evaluation will make them of continuing importance as verification tools for the more complex iteratively coupled codes.

3. REACTION KINETICS

The assumption of local equilibrium in most solute transport models is also present in the more sophisticated coupled geochemical flow models constructed today. Although this is an obvious theoretical weakness the practice continues for three reasons:

- It has so far been possible to simulate many systems of interest with the simple equilibrium approach. Thus there has been little incentive to develop kinetic reaction terms.
- The rate constants required for kinetic models are rarely available, although studies of geochemical reaction kinetics are beginning to appear in the literature (Aagaard and Helgeson, 1982; Reddy et al., 1982; and Rimstidt and Barnes, 1980).
- Most of the geochemical mass transfer models that could be chosen for coupling with flow models do not have the capability to consider rate controls on the reactions they simulate. Notable exceptions to this statement are the reaction path codes developed by Helgeson and his colleagues and the EQ6 code of Wolery (1979). Given sufficient rate data these codes could provide rate-controlled reaction descriptions if coupled to flow codes.

The limits to the equilibrium assumption have been explored in some detail in the literature of chemical processing engineering. In the earth sciences field Palciauskas and Domenico (1976) attributed apparent over saturation of groundwater in a carbonate aquifer system to calcium reaction rates being fast with respect to transport (equilibrium assumption holds for calcium) while magnesium reaction rates were slow with respect to transport (equilibrium assumption invalid for magnesium).

James and Rubin (1979) described a study of ion exchange in a column in which the fluid flow rate was varied to determine when the equilibrium assumption was no longer valid. They reached the very restrictive conclusion that the equilibrium assumption is valid only when molecular diffusion is about the same as or larger than the mechanical dispersion induced by flow. This conclusion seems at variance with the number of studies that have successfully simulated transport using the equilibrium assumption in systems with flow rates so high the James and Rubin criteria could not possibly be true.

It is clear that testing the validity of the equilibrium assumption is an area in which considerable further work is required.

4. EFFECTS OF CHEMISTRY ON FLOW

The remaining assumption limiting the present generation of solute transport models is that flow in the system is independent of chemical changes that take place. The parameters in equation (1) for water flow that could be affected by chemistry are the intrinsic permeability of the medium (κ), which could be changed by mineral solution and (or) precipitation, the viscosity (μ) and density (ρ) of the fluid, which will vary with total solution concentration, and the fluid pressure (p), which could respond to osmotic effects. The matrix porosity (ϕ), which appears in the transport equation (3), could also be affected by such chemical changes as mineral solution and (or) precipitation. This coupling is not normally included in solutions to that equation.

4.1 EFFECTS ON FLUID PROPERTIES

In the flow calculations for transport models intended to simulate isothermal laboratory experiments or shallow groundwater systems, constant matrix and fluid property values are used. Models for groundwater flow itself, intended for use in deeper systems and at more than one temperature, explicitly consider the pressure and temperature dependence of fluid density and viscosity. The resulting equations require numerical solution.

Several models of the transport of salinity have been built to simulate salt-water intrusion, for example, or the movement of fluid of one salinity injected into a groundwater of another (Bredhoeft et al., 1976; INTERA, 1983c). In these models density is expressed as a function of salinity, as well as of pressure and temperature, and viscosity as a function of salinity and temperature. Salinity is simply a dimensionless concentration such as the normalized concentration of total dissolved solids, or of chloride or NaCl, for example, against which density and viscosity variations are expressed (Muller et al., 1981). While salinity is transported, it does not undergo any reactions and from that point of view even in these models there is no back coupling of chemistry to flow.

4.2 EFFECTS ON MATRIX PROPERTIES

The intrinsic permeability and the porosity are matrix properties and will certainly be affected by changes in the matrix brought about by such chemical processes as precipitation and dissolution. In spite of the obvious need to consider such a coupling, no model is known that considers the influence of chemistry on intrinsic permeability or porosity.

The good reason for this omission is the lack of an acceptable theoretical or engineering procedure for calculating macroscopic intrinsic permeability values from the changes in the microscopic properties of a porous medium. A chemical model will give the changes in the mineral masses per volume element, which could easily be translated into a change in total porosity. A number of equations have been proposed relating porosity to permeability, some empirical, some based on idealized matrix particle geometries. Freeze and Cherry (1979, Section 8.7) discussed the problem, and Lerman (1979, Table 2.1) provided a list of a number of equations that have been proposed. None of these equations have received wide acceptance.

An adequate conceptual model for the effect of chemical changes on flow in fractures may be less difficult to develop than one for porous media, because an accepted expression for fracture permeability in terms of rock properties does exist. The intrinsic permeability of a unit volume of fractured rock can be written (Norton and Knapp, 1977):

$$\kappa = \frac{n(2b)^3}{12} \qquad (9)$$

where $2b$ = fracture aperature (m)
n = fracture frequency (m^{-1})

The porosity through which this flow occurs is the ratio of the volume of the fractures to the total volume and equals $n(2b)$.

Norton and Knapp (1977) examined the porosity characteristic of a number of fractured rocks. They found that while the total porosities ranged from 1 to 20%, diffusion porosities were in the range of 0.1 to 0.001%, the same range as is generally taken to be representative of the flow porosities in fractured rock. These small porosities suggest that the volumes of solids precipitated or dissolved in a fractures system need not be large to change a fracture aperture (2b) by enough to significantly affect flow rate. Experiments reported by Witherspoon et al. (1980), undertaken to verify equation (9), also illustrate that only small bulk rock volume changes are required to significantly change κ.

Chemical modeling in dual porosity media may require explicit consideration of two types of reaction sites. In the pores, where diffusional transport dominates, reaction times may be relatively long and permit the use of equilibrium-controlled reaction models. In the fractures, however, where convective transport dominates, reaction times may tend to be so short that kinetically controlled reaction models will be required.

Whether an equilibrium or kinetically controlled model is required for a given system may be explored as is done in chemical process engineering, by making use of the dimensionless Damkoehler groups I ($=kL/V$) and II ($=kL^2/D$) (Palciauskas and Domenico, 1976), which represent the ratios of chemical reaction rates to convective mass flow rate and to diffusion mass flow rate, respectively. In evaluating these ratios, the lengths and areas (L and L^2) will be characteristic of the block sizes used to solve the problem; V will be related to the tracer velocity in the fractures (Darcy flux/flow porosity) and D to the diffusivity of the medium (molecular diffusion coefficient/diffusion porosity/tortuosity). Representative reaction rates (k) will be the most difficult terms to evaluate, but, as mentioned in Section 3, some reaction rate data are beginning to appear.

4.3 EFFECTS ON PRESSURES

Chemical changes could also influence the fluid pressure (p) in equation (1), through such mechanisms as mineral hydration or dehydration reactions or osmotic effects. No attempt has yet been made to include these mechanisms in any chemical and flow models, but they have received attention from hydrogeologists and geochemists (Graf, 1983; Hanshaw and Bredehoeft, 1968; Marine and Fritz, 1981). Although their operation could have a profound effect on pressure, they are not likely to be common and so their neglect should cause no general difficulty.

5. SUMMARY

Present solute transport models fall short of being coupled geochemical and flow models in one or more of the following areas:

- Geochemical reactions are treated simplistically, if at all;
- Reactions are commonly modeled as equilibrium controlled; and,
- Chemical effects on fluid flow are usually neglected.

More realistic chemistry can be included by:

- Directly coupling transport equations written for individual reacting species for specific reactions; or
- Iteratively coupling geochemical reaction models to a flow model.

Iteratively coupling will provide general codes, but they will require verification against theoretically more rigorous directly coupled models.

The assumption of equilibrium controlled reactions will remain a practical necessity for most problems until the body of geochemical reaction rate data increases.

The effect of chemical reactions on fluid properties and on rock porosity can be calculated . The effect of porosity changes on the changes of hydraulic conductivity in porous media is not known, however, so modeling the effects of chemical changes on flow will remain empirical.

In fractured rock, different reaction models may be needed for the fractures themselves, where relatively rapid convective transport dominates, than for the intervening porous media where slower diffusion processes will control transport.

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DISCUSSION

It is presently feasible to construct a fully coupled computer model linking geochemistry and fluid and heat flow. Such a model should have modular representation of the several processes involved to permit straightforward improvement of process descriptions in response to data base improvements, theoretical advances, problem-specific needs, etc.

Such a model, if available now, would have the following shortcomings:

(1) Computers with sufficient size and speed to run the model efficiently are not widely available. Useful problems on commonly available machines would require long run times and hence be very expensive.

(2) Although the model would be based on general algorithms, data availability will limit its use to restriced sets of problems. [Refer back to Greenwood/Brown and Skytte Jensen Sessions].

(3) Problem sets for which kinetic data are available will be even more restricted.

(4) Data on the effect of changing porosity or fracture configuration on intrinsic permeability are lacking.

The second and third shortcomings will more seriously limit its near-field use than its far-field use.

The utility of such a model in high-level waste programs would outweigh its shortcomings and we recommend beginning its construction immediately. It will be important even in early stages of development for such tasks as:

- Sensitivity analysis
- Rational selection of simplifications for inclusion in models for routine use.

As data needs are met and improved computers become available, it will become useful as well for site problems.

SIGNIFICANCE OF MICROBIOLOGICAL ACTIVITY AND GROUNDWATER REDOX POTENTIAL IN CONTROLLING NUCLIDE RELEASE AND MIGRATION PROCESSES

J.F. Barker

1. INTRODUCTION

Nuclide release and migration from a disposal site are functions of both geochemical and physical transport processes. Predictive models require knowledge about the rates or extent of solid phase and aqueous phase interactions such as sorption, precipitation and dissolution. This, in turn, requires evaluation of aqueous speciation and solid phase composition.

Microbes form part of the solid phase, both fixed and transported as particles or colloids, and so influence the inter-phase distribution of nuclides. Most dissolved constituents can exist in more than one chemical form or species. This speciation is a function of concentrations and various environmental factors including temperature, pH and Eh or pe (redox potential). In many groundwaters, microbiological activity influences this aqueous speciation, especially for redox-sensitive (multi-oxidation-state) nuclides.

Microbiological research programs are underway or anticipated in both North America and Europe including Canada, United States, United Kingdom, France, Italy and Switzerland.

2. POTENTIAL MICROBIOLOGICAL PROCESSES

These processes are arbitrarily divided into "direct" and "indirect" categories on the basis of the perceived directness of their influence on release and migration of nuclides. Direct processes include:

(1) microbial contribution to container or waste-form deterioration,

(2) fixation of nuclides by microorganisms, and

(3) generation of aqueous, organic ligands capable of complexing and so influencing nuclide speciation.

Indirect processes include microbial influences upon:

(1) Eh and pH which affect nuclide speciation, and

(2) solid surfaces which affect inter-phase transfers.

Hopefully, any additional areas of concern will be presented during the workshop.

Instances of direct microbial attack on materials (such as glass, concrete, metals, bitumen) considered for waste containers are well documented. Durability experiments are required under conditions anticipated in the disposal situation before the extent of such attacks can be assessed. The effects of high termperature and radiation flux, in particular, could restrict microbial involvement in material deterioration.

All microorganisms incorporate some trace metals into their cell mass in order to carry out metabolic processes. Therefore, uptake of nuclides of such metals, and perhaps geochemically similar metals, is possible but poorly documented in the literature. Nuclide uptake by non-motile species would retard nuclide migration, whereas uptake by motile species may not be as significant a retardation factor. Although useful directions may be gained from a review of the literature, prediction of rates of uptake and release can only be obtained from realistic experiments.

Microbial materials, including extracellular excretions, have a potential to sorb nuclides, perhaps reversibly. Although the interaction of cations with certain specific organic molecules is well documented, the interaction with large, complex life substances such as proteins and carbohydrates is poorly understood. Before extensive studies of this possible interphase transfer process are undertaken, their relative importance should be assessed vis-a-vis mineral surface sorption.

Microbial processes in groundwater alter its organic geochemistry. Since many of the molecules produced or consumed are potential ligands for metals or cationic nuclides, microbial processes have a direct bearing on the aqueous speciation of those nuclides. For inclusion of such ligands in predictive speciation models, both their identity and concentration must be specified. Unfortunately, the bulk of organic matter in groundwaters defies unique identification. For example, although groundwaters from crystalline terrain in Sweden contained up to 20 μg/L dissolved organic carbon (DOC), only a few mg/L of specific organics could be identified (Means, 1982). Our studies indicate that organics in groundwaters containing up to 15 μg/L DOC can complex up to about 10^{-5} equivalents of metal per litre, so it seems important to include organic ligands in some manner in speciation models. This will become considerably less important in systems lower in DOC. Unfortunately, many backfill/buffer materials contain leachable or microbially-usable organic matter and so the near-field may contain significant organic ligands. Perhaps the backfill/buffer materials should be the focus of organic-nuclide interaction research.

Microbial activity exerts an indirect control on nuclide release and migration through involvement in redox and acid-base reactions. Redox (oxidation-reduction) processes influence multioxidation-state nuclides such as ^{79}Se, ^{129}I, ^{238}U, ^{237}Np and ^{238}Pu; acid-base processes are important where hydrolyzed species such as $U(OH)_2^+$, $U(OH)_3^+$, and $U(OH)_4^0$ can form.

Microbes have been treated as catalysts in the sequential disappearance of oxidized species commonly observed along groundwater flow systems. The order of disappearance and approximate redox potential (Eh) for each reduction can be predicted with the aid of equilibrium thermodynamic principles. The microbial involvement becomes critical when the time-dependency of Eh is included in models. Although the microbiological factors influencing these rates are generally appreciated, the prediction of rates under presumed conditions is not currently possible.

An interesting aspect of microbiological control of redox conditions is the possibility of enhancing microbial activity in order to hasten the onset of anoxic, reduced conditions in the disposal environment if such conditions do, in fact, minimize nuclide release and migration. Research into such action must not only evaluate the means of enhancing microbial activity but also consider possible deleterious consequences of this activity including sulphur oxidation, producing acidic conditions and the generation of soluble organic-nuclide complexes, which would enhance nuclide migration rates.

In a shallow sand aquifer, 10^6 to 10^7 viable bacteria per gram were found on the porous media while only 10^2 to 10^3 bacteria per cm^3 were found in the groundwater. Microorganisms concentrate on surfaces. Establishment of a significant biofilm along conducting fractures would greatly alter the interphase transfers affecting released nuclides. Biofilm development is dependent upon nutrient levels (and other factors) and in most disposal scenarios would not be significant. It may be advantageous to promote biofilm development and thus clogging of fractures and perhaps enhanced nuclide "sorption". This possibility should be assessed in the overall evaluation of the advisability of enhancing microbial activity in the disposal site.

3. THE POTENTIAL FOR MICROBIAL ACTIVITY IN THE FAR-FIELD

Very little microbiological data exists for low permeability, granitic rocks. One reason is the lack of adequate sampling protocols for obtaining an uncontaminated, representative sample of the in situ microbial population. Literature reviews (e.g., Mayfield and Barker, 1982a; McKinley and West, 1983) summarize the requirements for microbial activity and conclude that granitic rocks should contain viable microorganisms. Recently this was confirmed when viable, salt-tolerant, aerobic and facultative anaerobic bacteria were found in groundwater flowing from an underground exploration borehole. Major research efforts will be required to establish the nature of the natural microbial population. Before such effort is undertaken it must be rationalized. As discussed in the next section, the microbial and geochemical influence of the near-field may dominate the far-field microbial processes. In that case, relatively little benefit may be realized at high cost in attempts to identify the natural microbiological population.

4. THE POTENTIAL FOR MICROBIAL ACTIVITY IN THE NEAR-FIELD

Some natural clay backfill/buffer materials have significant microbial populations (10^3 to 10^6 bacteria per gram; Mayfield and Barker, 1982b) and mixtures of these with saline, organic-free waters support some growth. Addition of nutrients, especially organic carbon, increases microbial activity dramatically and can rapidly bring about anoxic, reducing conditions. These materials should be studied especially for consideration of "engineering" desired redox conditions. In the disposal environment, the major limitation to microbiological growth should be high temperature and high radiation flux and so these conditions should be considered in future experiments. It is generally concluded that temperature in excess of 90-100°C and an acute radiation exposure of 10^5 - 10^6 rads* will inhibit almost all microbial activity but may not destroy resistant spores or dormant forms. Recent experiments (Baross and Deming, 1983) suggest this maximum temperature may be 250 to 350°C.

5. GROUNDWATER REDOX POTENTIAL

The prediction of redox potential in granitic groundwaters at proposed disposal depths is not possible at this time due, in part, to the lack of data. Many current projects are evaluating Eh in such groundwaters so the data base is growing. In most active groundwaters, redox potential decreases along the flow system and over time, in major part due to microbiological processes. Quantitative prediction of rates, however, is not possible. For much longer periods of time, geochemists often invoke the control or buffering of Eh by naturally occurring couples such as magnetite (Fe_3O_4) and hematite (Fe_2O_3). This buffer may operate to maintain reducing conditions in granitic rocks since magnetite is a common granitic mineral. However, there is little indication that this buffer does control Eh in granitic systems studied to date. This could be due to the well-documented problems with electrochemical measurement of Eh under reducing conditions.

Manipulation of the backfill/buffer materials and perhaps also microbiological activity therein could be considered to provide rapid reduction via microbial reactions and to maintain reduced conditions through the provision of reducing agents such as Fe (II) minerals. Migration of contaminated groundwaters from the disposal site may then maintain these reducing conditions through most of their subsequent flow. In this scenario, extensive redox surveys of granitic groundwaters may not be critical to the prediction of nuclide migration.

Does the measured Eh provide a reliable means of assessing the relative proportions of oxidized and reduced species? Rarely have measured Eh values coincided with redox potentials calculated from redox couple determinations such as As (V) - As (III), SO_4^{2-} - HS^-, HCO_3^- - CH_4. The reported non-equilibrium redox distributions of plutonium also suggests that a measured Eh may not permit confident calculations of redox-sensitive species. Also, organically complexed Fe (II) can apparently be "protected" from oxidation to Fe (III) even when oxidizing conditions are encountered. Unfortunately, there does not appear to be a better approach to the prediction of redox-sensitive speciation in groundwaters.

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* 1 rad = 10 mGy

6. SUMMARY

Microbiological activity will occur in both the far- and near-field disposal environments except where high-temperature and high-radiation flux exist. Activity levels and precise geochemical results cannot be defined at present. Both detrimental and beneficial consequences are possible and these must be better defined, especially if encouragement of this activity is considered. In some situations, the microbiological activity in the near-field may so dominate far-field activity that the difficult research in far-field studies may not be justified.

Prediction of redox conditions during nuclide release and migration cannot be made precisely but gradual lowering of Eh is anticipated. Buffering by reduced iron minerals is possible. The problems of both measurement of Eh and prediction of speciation of redox-sensitive nuclides using solution Eh data are well recognized and may greatly limit the precision of aqueous speciation models.

DISCUSSION

1. Although realistic experiments with mixed populations under appropriate environmental conditions should be emphasised, some experiments under relevant but idealised conditions should be considered in order to define constraints on important microbial processes.

2. Research programmes should emphasise the constraints on microbial processes rather than attempt to include all possible microbial effects in geochemical models. Continued effort is urged to delineate these critical microbial processes.

The microbiology of pristine crystalline environments, although of potential importance, does not appear to warrant the major research effort required. However, research into analogues for the post-mining, pre-closure behaviour of the repository would be essential to define the environmental conditions upon closure. These will influence post-closure behaviour, particularly microbial processes. Microbial research of flooded undisturbed mines is recommended.

3. Experiments should be conducted at realistic temperatures and radiation fluxes with consideration of mutation included.

4. Development of cell mass on fracture surfaces (biofilms) could greatly influence the adsorptive properties of the surfaces. Although some general information exists in the literature, detailed realistic experiments of sorption by biofilms would be required.

5. Uptake could include a number of complex processes including sorption of nuclides onto extracellular materials such as iron oxyhydroxides.

6. Complexed nuclides of metals may be soluble and promote migration or may be insoluble and promote retardation. These complexes may evolve geochemically and their solubility relationships change over time. These complexes may be regulated by microbial activity.

7. The microbiological consequences of radiolysis, especially the potential generation of oxidised species, should be evaluated as radiolysis research continues.

8. Space constraints, especially with compressed bentonite backfills, will certainly inhibit microbial mobility and may prove to be a significant constraint on microbial activity.

9. Experimentalists should be aware of potential microbial activity. It is impossible to conduct sterile experiments, but with suitable precautions such effects could be minimised.

10. To effectively undertake this microbial research, given the limited available resources, a coordination of the programmes of individual agencies is essential. Although individual initiative should not be stifled, collaborative interaction with timely exchange of information should be encouraged.

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OPEN SESSION

The following papers are extended personal comments from individual participants who wished to bring forward subjects they considered newsworthy and relevant to the main body of the discussions. As such they may reflect in places the author's own views rather than those of the workshop as a whole. They are thus included here separately from the discussion papers and their accompanying consensus summaries. Note that the following papers were also presented, but the texts are not available:

"Dissolution Kinetics of Albite at 25 and 70°C" by Dr. T.J. Wolery.

"An Overview of Geochemical Aspects of U.S.A. Salt Program"
by Dr. J.B. Moody.

"Technical Input to Repository Siting" by Dr. J.O. Duguid.

THE COMMISSION OF EUROPEAN COMMUNITIES PROJECT "MIRAGE" (MIGRATION OF RADIONUCLIDES IN THE GEOSPHERE): AN OVERVIEW

B. Come

1. INTRODUCTION

The co-ordinated project "MIRAGE" on Migration of Radionuclides in the Geosphere corresponds to the follow-up, from 1983 onwards, of the present activities of the laboratories of the Member States, up to the end of 1984, and of the Joint Research Centre at Ispra, up to the end of 1983. It is concentrated upon the study of the transfer of radioactivity from conditioned waste through the different barriers up to the interface between the geosphere and the biosphere.

The MIRAGE project is performed in the framework of the Commission of European Communities (CEC) indirect action programme on Management and Storage of Radioactive Waste, sub-programme Underground Disposal, and of the CEC direct action programme on Safety of Nuclear Materials at the Joint Research Centre, Ispra Establishment.

The total financial commitment in this project is at present 6,384,000 ECU for 1983 and 1984 and the Commission participates financially in each study selected on a cost-sharing basis to a level of about 40% of the total cost. The costs of the studies performed at JRC-Ispra are not included in this amount.

The number of organizations, firms and laboratories involved in this project comes to about 40.

2. RATIONALE OF THE MIRAGE PROJECT

Migration studies up to now have allowed the clarification of certain aspects of migration phenomena. However, the laboratories concerned are coming up against many difficulties at present, due mainly to the great number of chemical or physical variables involved on the one hand, and on the other hand, the problems of establishing representative models allowing the global understanding of the radioactivity transfer mechanisms as well as their quantification.

The problem of producing useful results in a reasonable time can be overcome to a large extent by concentrating on site-specific studies, where the materials and environments involved can be tightly quantified. Concentration on a limited number of sites will allow parallel development of a generic understanding of mechanisms, and the production and updating of pertinent data for modelling. It is this approach that forms the basis for this Community project.

Assuming that a reasonable background knowledge exists of flow parameters, rock properties and geological environment, the principal factors required to set up migration models are the release source term for the waste type under consideration and the retardation processes occurring during transport.

3. SALIENT FEATURES OF THE MIRAGE PROJECT

Since the project emphasizes the importance to be attached to integrated, site-specific studies, investigations are centred on four Community reference sites: Limousin (F) and Cornwall (UK) for granite, Mol (B) for clay and Gorleben (D) for salt.

The laboratory investigations deal with a few representative radionuclides. These nuclides, constituting the source term, are chosen taking into account the amount present in the waste form, as well as the radiotoxicity of the individual isotopes.

Only four radionuclides are studied in the programme:

- Tc, representative for long-lived fission products;
- Am, Pu, Np, representatives for actinides.

For experiments involving waste forms, the wastes are representative of the LWR fuel cycle. Three reference matrices are used:

- for high-level reprocessing waste, the French borosilicate Marcoule-Cadarache doped glass R7 T7;

- for intermediate-level waste, an actual reprocessing concentrate in cement (WAK-Karlsruhe) and a real reprocessing sludges incorporated in bitument (CEA-MAR).

Common samples of these materials are made available to the laboratories involved.

4. RESEARCH AREAS AND BREAKDOWN OF THE ACTIVITIES

For operational purposes, seven key research areas are defined:

1. Basic Actinide and Fission Product Chemistry
2. Integral Simulation Experiments
3. Laboratory studies related to specific sites
4. Hydrogeology
5. Natural Geological Migration Systems
6. Micro-organisms
7. Development of calculation tools.

It is considered that these topics will provide the specific data needed, and the results obtained will be used to set up migration models.

4.1. Basic Actinide and Fission Product Chemistry

The objective is to produce thermodynamic and kinetic data needed for understanding and predicting, for a given set of conditions, the behaviour of radionuclides and for modelling their migration in the geosphere.

The experimental investigation is focussed on the following aspects:

- Basic solution chemistry (solubility, carbonate and hydroxide complexes, kinetics and development of speciation techniques);
- Colloid behaviour;
- Sorption phenomena.

Particular attention has been paid on solubility and speciation studies, including colloid formation and characterization in salt rock systems (TU-München and JRC-Ispra), in granitic waters (CEA-FAR), and in clay waters (JRC-Ispra). Other studies are dealing with basic retention mechanisms of isomorphous substitutions in salt rock and multi-element ion exchange in clay components (Risø and CEA-FAR).

4.2. Integral Simulation Experiments

The objective is to perform laboratory simulation experiments in order to determine the migration pattern of radionuclides leached from the waste form. These experiments, in combination with the output of the basic solution and sorption chemistry studies, should allow the development of more realistic models of radionuclide migration in the geosphere.

Several laboratory simulation experiments (flow-through column experiments, with possible supporting static batch experiments) are defined in order to identify the main processes occurring during the radionuclide transfer under representative conditions. The nature of the waste forms representing the reference matrices and the chemical environment typical of the different disposal options are considered.

For HLW, one experiment will be supervised by CEA-Cadarache involving granite and clay systems; CEA-MAR will participate in this action by performing some basic experiments. Experiments will be performed by JRC-Ispra for the salt environment.

As the techniques involved are quite similar, a close liaison between the leading laboratories in experimental design is essential.

Supply of common test materials will be carried out by CEA-MAR, KfK and possibly by JRC-Ispra.

4.3. Laboratory Studies Related to Specific Sites

This research mainly intends to back-up large-scale field experiments performed in research area 4 on hydrogeology, and to provide mechanistic data to be used for modelling migration phenomena.

The effort will concentrate on an investigation of migration phenomena in a mixed sedimentary sequence (Mol) with less of an effort on a single-fracture migration experiment in granite (Cornwall).

The work at Mol is supervised by CEN-SCK and BGS is participating. The objectives of the work are to characterize pore water chemistry and diffusion/retardation phenomena in clay and to study the migration processes in the overlying aquifer sediments. These objectives will be achieved by co-ordinated laboratory experiments on samples from the Mol site and possibly by an in-situ migration experiment, in a subsequent phase.

The work in granite consists of supporting laboratory studies for preparation and interpretation of the UKAEA single fracture experiment (Cornwall); the field experiment in Canada by AECL/UKAEA is the subject of the work performed at UKAEA-Harwell.

4.4. Hydrogeology

It is generally admitted that possible transport by mobile groundwaters would be one of the most likely processes whereby deep disposed radionuclides return to man's environment. The forecast of such a transport necessitates the knowledge of information that characterizes both the movement of groundwaters and their physical and chemical properties.

Two central areas of research are being investigated, involving studies of crystalline rock and sedimentary rock hydrogeology.

Work on sedimentary rock hydrogeology is co-ordinated by CEN-SCK and concentrates on the characterization of the regional flow pattern in the sedimentary sequence in the Mol area. Techniques and results should be widely applicable to mixed sequences elsewhere in the Community. A supporting study of natural series isotope equilibria in groundwater systems will be performed by UKAEA at the Mol site.

The second area (crystalline rocks) is centred principally on a CEA/BRGM/EMP project for large-scale tracer tests in an underground facility in granite. A limited effort is also made in the scope of the AECL/CEC co-operation programme, involving studies by BGS and UKAEA of hydraulic/hydrochemical properties and groundwater dating, respectively.

The granite single-fracture migration experiment will validate models of pore diffusion and fissure flow as well as colloid transport, and will be operated by UKAEA.

4.5. Natural Geological Migration Systems

The objective is to study particular geological structures, in which migration phenomena of some representative natural elements have been active during very long time spans. At the end of the studies, one should be in a position to validate some predictive migration models developed for the disposal of radioactive waste.

For fractured media, a comparison will be made on natural and disposal-induced hydrothermal alteration; the potential for radionuclide "trapping" will be determined from the behaviour of natural analogues (e.g., rare earths) (BRGM). On the other hand, a data collection will be performed on natural ore deposits, with a view to establishing analogies between the weathering of these deposits and the long-term evolution of radioactive waste repositories (BRGM).

For clay, a study of natural long-term (10^3 - 10^4 years) elemental migration in a sedimentary sequence will be performed in the UK (BGS). Some support will be given by a study of the changing redox conditions affecting the superficial part of an Italian clay layer (ENEA).

4.6. Microorganisms

Several recent literature searches have shown that microorganisms are known to exist in particular geological formations, at depths of up to 5 km, and to tolerate very extreme environmental conditions (e.g., high pressure, temperature, radiation, salinity, etc.). In addition, a variety of microorganisms will be introduced to groundwater systems during water chemistry, and processes related to it must be taken into account in the evaluation of repository behaviour. To date, however, very little microbiological research has been focused on geological formations relevant to the nuclear waste management progamme or on the evaluation of the possible consequences of microbial populations on repository integrity or the transport/retardation of released radionuclides.

The particular aims in this research area are:

- to identify and quantify both those microbial populations naturally present in geological formations relevant to the deep disposal of radioactive wastes (CEA), and those microorganisms that might be introduced during repository construction and operation (BGS);
- to evaluate the possible effect of such organisms on radionuclide migration through the geosphere.

4.7. Development of Calculation Tools

The aim of these activities is to consider the development and application of suitable calculation tools to problems of groundwater flow, solute transfer and coupling of geochemical/flow models. These activities should result in:

- the development of computer codes for application to the specific sites selected for the project (laboratory and field experiments) on the one hand, and the so-called integral laboratory experiments on the other hand;

- the development of techniques for the eventual coupling of geochemical and groundwater flow models.

Research items are categorized as follows:

- Source-term problems, i.e., production and characterization of leachates from the waste (JRC-ISPRA);
- Water flow modelling (UKAEA, CEA-EMP, CEN/SCK, R.I.D.);
- Phenomena related to heat propagation in the host formations (e.g., convective thermal currents, etc.) (CEA-EMP, CEN/SCK);
- Geochemistry/Thermodynamics, i.e., mainly groundwater/rock interaction pehenomena occurring during groundwater flow (RISØ);
- Hydrodynamic dispersion phenomena (CEA/EMP);
- Nuclide migration/retardation process (UKAEA, BGS, RISØ);
- Coupling of the above-mentioned items (CEA/EMP, BGS).

These items are relevant for both fractured media (e.g., granite) and porous media (clays and sediments). In addition, a preliminary validation of selected computer codes will be undertaken (ATKINS R&D).

LIST OF ABBREVIATIONS

ATKINS:	Atkins Research and Development, Epsom, U.K.
BGS:	(formerly IGS), British Geological Survey, Keyworth, U.K.
BRGM:	Bureau de Recherches Géologiques et Minières, Orléans, France.
CEA-FAR:	Commissariate à l'Energie Atomique, Fontenay-aux-Roses, France.
CEA-CAD:	Commissariate à l'Energie Atomique, Cadarache, France.
CEA-MAR:	Commissariate à l'Energie Atomique, Marcoule, France.
CEN/SCK:	Centre d'Etude de l"Energie Nucléaire, Mol, Belgium.
EMP:	Ecole des Mines de Paris, Fontainebleau, France.
ENEA:	Comitato Nazionale per la Ricerca e lo Sviluppo dell'Energia Nucleare e della Energie Alternative, Romas, Italy.
FU Berling:	Freie Universität Berline, Federal Republic of Germany.
JRC ISPRA:	Joint Research Centre, Ispra, Italy.
KfK:	Kernforschungszentrum Karlsruhe, Karlsruhe, Federal Republic of Germany
R.I.D.:	Rijksinstituut voor Drinkwatervoorziening (National Institute for Water Supply), Leidschendam, The Netherlands).
RISØ:	Risø National Laboratory, Roskilde, Denmark.
TU MUNCHEN:	Technische Universität München, Garching, Federal Republic of Germany.
UKAEA:	United Kingdom Atomic Energy Authority, Harwell, U.K.

INFLUENCE OF THE INTERACTION BETWEEN FLUID AND ROCK ON THE CONVECTIVE FLOW IN FRACTURES*

G. de Marsily

INTRODUCTION

In this paper, some results are presented on the convection flow in the fractures of a rock massif. We shall study successively the relationship between buoyancy flow and the geometry of the medium, and next the phenomena of dissolution and precipitation from the solution flowing in the direction of a temperature gradient.

NATURAL CONVECTION

Density differences due to temperature or concentration variations can induce motion in a fluid. The studied configuration is a rock massif with vertical faults (Fig. 1).

If a horizontal gradient of density exists as, for example, near a horizontally limited heat source, the configuration is intrinsically unstable. Whichever power is dissipated, if the hydraulic characteristics of the fracture allow it, two convection cells will appear (Fig. 2).

In the case of a vertical gradient of the temperature, natural convection appears above some critical gradient. One generally uses the adimensional Rayleigh number to characterize the instability of the configuration:

$$Ra^x = \frac{k_f \gamma \beta \rho g \alpha H^2}{\mu \lambda^x}$$

The critical value of this number, above which the motion appears, depends on the geometry of the fractures and on the characteristics of the rock. Assuming that the equations are linear for small perturbations and that the thermic perturbation due to the natural convection is sinusoidal in both directions of the fracture plane, one can find the following expressions of the critical Rayleigh number Ra_c^x versus the shape ratio F of the fractures and versus the number n of cells that appear:

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* Previously presented by A. Ribsteine and E. Ledoux at Conférence de recherches: "Phénomènes thermiques dans les bassins sédimentaires" Institut Francais du Pétrole, Université de Bordeaux I, Société Francaise des Thermiciens, Bordeaux, Juin 1983.

$$Ra_c^X = \frac{n^2+F^2}{n^2\ F^2}\ (\pi^2(n^2+F^2)+\ \Phi)\ \text{pour}\ F_1(n-1) < F < F_1(n)$$

with $$F_1(n) = (\frac{\Phi^2+4\pi^2n^2(n+1)^2-\Phi}{2\pi^2})^{1/2}$$

Figure 3a illustrates these expressions. When the thermal flux Φ between the fissures and the rock matrix increases, or when the horizontal extension increases, then Ra_c^X increases too and the configuration becomes more stable. For large horizontal extensions of the fissures, the crit. Rayleigh number tends towards $4\pi^2$ and the number of convection cells tends toward the ratio F of the figure.

A numerical model solving the coupled equations of the fluid transfer in the fissures, and of the heat transfer both in the fissures and in the rock matrix, has been constructed with assumptions less restrictive than in the preceding results (Fig. 3b). They also show that the number of convection cells increases when the Rayleigh number becomes largely greater than its critical value, and they show that an increasing influence of the rock matrix reduces the speed of the fluid and the number of cells (Fig. 4).

GEOCHEMICAL INTERACTION FLUID-ROCK

The solubility of minerals depends on the temperature, so the chemical composition of a solution flowing in the fractures of a rock massif varies with the temperature field. Precipitation or dissolution can occur and can modify the thickness of the fractures and then the motion of the fluid.

The studied configuration is represented by a one-dimensional model in the direction of the fluid motion (Fig. 5) into the fracture.

Assuming that the velocity of the fluid V and the thickness of the fissure e_f are constant, the equation of the mass balance for a given substance is:

$$\frac{\partial C_L}{\partial t} = -V\ \frac{\partial C_L}{\partial z} - r(C_L-C^x)$$

The kinetic coefficient r and the solubility C^x are functions of the temperature and then of the distance too. Using the following approximations:

$$r = g - fz \quad \text{and} \quad C^x = -az + b + he^{-lz}$$

where g, f, a, b, h and l are constant, one can find these analytic solutions:

$$C_L = f_1(t,z) \quad \text{and} \quad C_s = f_2(t_1,t_2,z)$$

where C_s is the precipitated or dissolved mass per unit of fissure volume between the dates t_1 and t_2, at the distance z from the origin where the concentration is imposed.

One can study the variation of these two functions versus any parameter. When the solubility and the kinetic coefficient decrease in the direction of the fluid motion, precipitated mass increases with time, with the imposed concentration at the origin, with the solubility gradient and with the velocity of the fluid.

Calculations were made to simulate the precipitation of amorphous silica in the neighbourhood of a radioactive waste disposal vault placed into a granitic massif at 1000 m depth. The geothermal gradient and the heat perturbation due to the waste are superimposed. In the studied case, this perturbation has a maximum of 15°C in the rock about 100 years after the waste is placed into the massif. A large range of the fluid velocity and of the kinetic coefficient was envisaged, and the calculations were discretized in time to take into account the evolution of the temperature field.

In the most favourable cases for the precipitation ($V = 10^{-5}$ m/s and $r = r_{M2}$), we obtain a mass per unit of fissure volume of 5.10^5 mg/L after 10 000 years. The silica density is d = 2.2, so the deposit thickness is, in this case, 0.23 times the fissure width.

CONCLUSION

The fluid included in the fissures of a rock massif is unstable when there is a horizontal gradient of temperature as, for example, near a horizontally limited heat source.

In the case of a vertical gradient as, for example, the geothermal gradient, the fluid is unstable above a critical value of this gradient. This value corresponds to the critical Rayleigh number and depends on the geometric, thermic and hydraulic characteristics of the medium. In general, the fluid is less stable as the fracture horizontal extension is larger compared to the vertical extension. When the fracture horizontal extension tends toward infinity, on the one hand, the critical Rayleigh number leads to $4\pi^2$ and, on the other hand, for a Rayleigh number slightly greater than this value, the number of convection cells becomes equal to the ratio of the horizontal extension of the fracture to the vertical one. Furthermore, when the Rayleigh number increases, the number of convection cells increases and the influence of the rock matrix tends to diminish the number of cells.

The evolution of a convective solution in contact with minerals in a medium where physical and geochemical parameters vary is very complex. We just solved analytically the balance mass equation of only one substance, in the case of a simple geometry and when only solubility and kinetic vary. The precipitated or dissolved mass is an increasing function of the fluid velocity and of the solubility gradient.

From these solutions, we calculated the thickness of the silica deposit in fissures intersecting a radioactive waste disposal in a granite massif. Taking only into account the temperature variation and its consequences on the solubility and the kinetics of dissolution, the sealing is not yet obtained after 10 000 years.

NOMENCLATURE

α	voluminal extension coefficient of the fluid	$K^{-1}L^{-3}$
β	vertical gradient of temperature	$K\ K^{-1}$
γ	heat capacity of the fluid	$K^{-1}L^{-1}M\ T^{-2}$
λ^*	heat conductivity of the fissure	$K^{-1}L\ M\ T^{-3}$
μ	dynamic viscosity of the fluid	$L^{-1}M\ T^{-1}$
ϕ	increasing function of the flux between fissure and rock matrix	
ρ	volumic mass of the fluid	$L^{-3}M$
ψ	stream line	L^2T^{-1}

C_L	concentration, C^* solubility	$L^{-3}M$
C_s	precipitated or dissolved mass per unit of fissure volume	$L^{-3}M$
e_f	fissure width	L
g	gravity	$L\ T^{-2}$
H	vertical extension of the fissure	L
k_f	intrinsic permeability of the fissure	L^2
L	horizontal extension of the fissure	L
r	kinetic coefficient	T^{-1}
t	time	T
V	Darcy's velocity of the fluid in the fissure	$L\ T^{-1}$
Y_L	half of the rock thickness between two vertical fissures	L

$F = \frac{L}{H}$	shape ratio of the fissure
n	convection cells number in L
Nu^*	Nusselt number equal to the ratio of the total thermic flux (convection + conduction) on the flux that would pass through the same horizontal section of the fissure by conduction only
Ra^*	Rayleigh number which critical value is Ra_c^*

$$Ry = \frac{2Y_L + e_f}{e_f}$$

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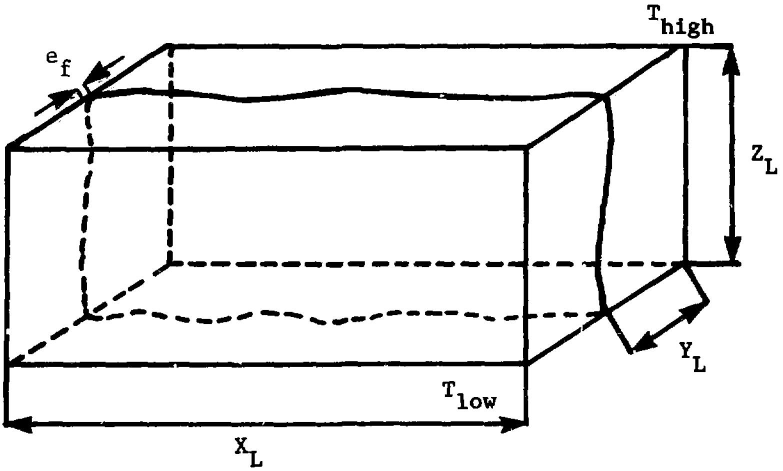

FIGURE 1: Studied Configuration. e_f: width of the fissure; $2Y_L$: distance between two fissures; X_L and Z_L: horizontal and vertical extension of the configuration; T_{high} et T_{low}: imposed temperature on the horizontal boundaries

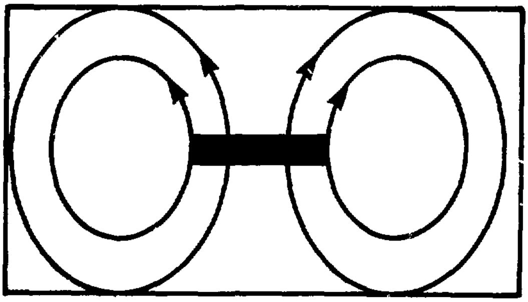

FIGURE 2: Streamlines in a Vertical Fracture Intersecting a Heat Source (in black)

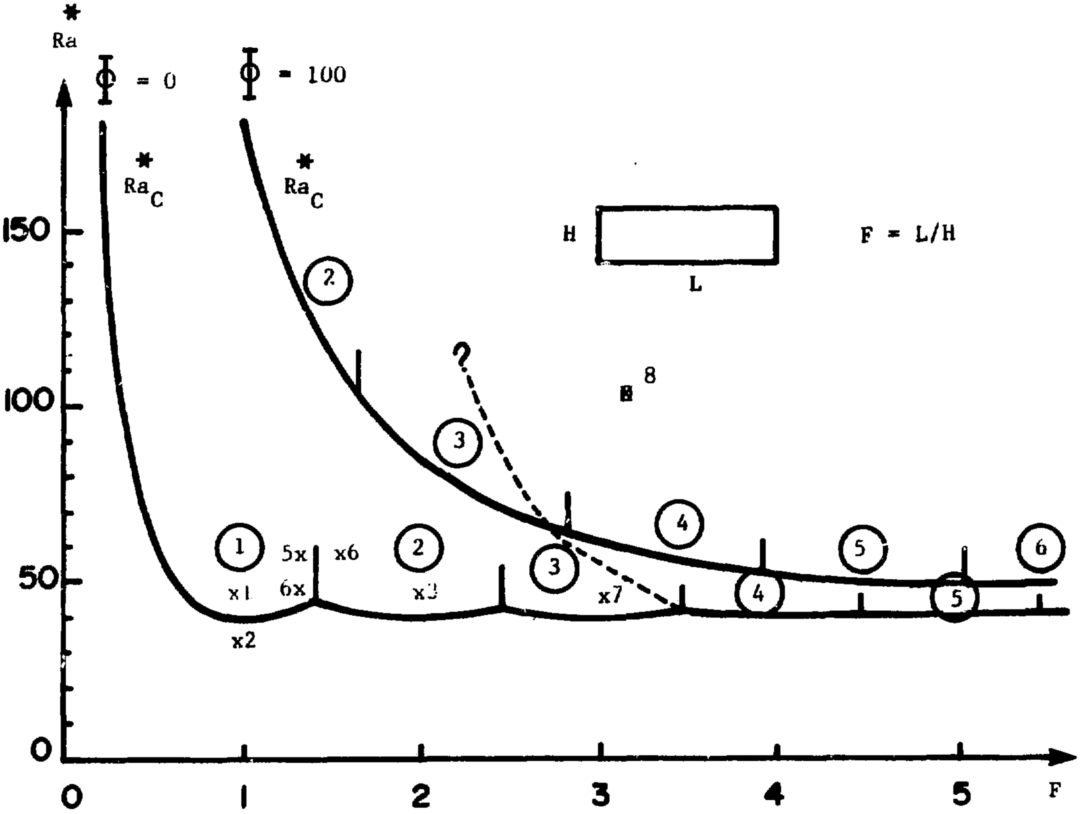

FIGURE 3a: Critical Rayleigh Number Versus the Shape Ratio of the Fissure. ϕ: increasing function of the thermal flux between the fissure and the rock matrix; 1: cells number; x2: simulation with fissure only; 0^8: simulation with fissure and rock matrix; dotted line is the probable boundary between 3 and 4 cells for ϕ = 0

Simulation	Ra*	Ra^*_c	F	R_y	n	Nu*
1	44.7	39.5	1	1	1	1.16
2	35	39.5	1	1	0	1
3	44.7		2	1	2	1.16
4	44.7	44.1	1.4	1	0	1
5	52	43.1	1.35	1	1	1.37
6	52	43.7	1.45	1	2	1.33
7	44.7	39.5	3	1	3	1.16
8 a	108	39.5	3	1	4	2.0
b		$39,5<Ra^*_c<108$		1.1	4	1.9
c				1.25	3	1.48
d				1.3	3	1.14

FIGURE 3b: Characteristics and Results Simulations Table

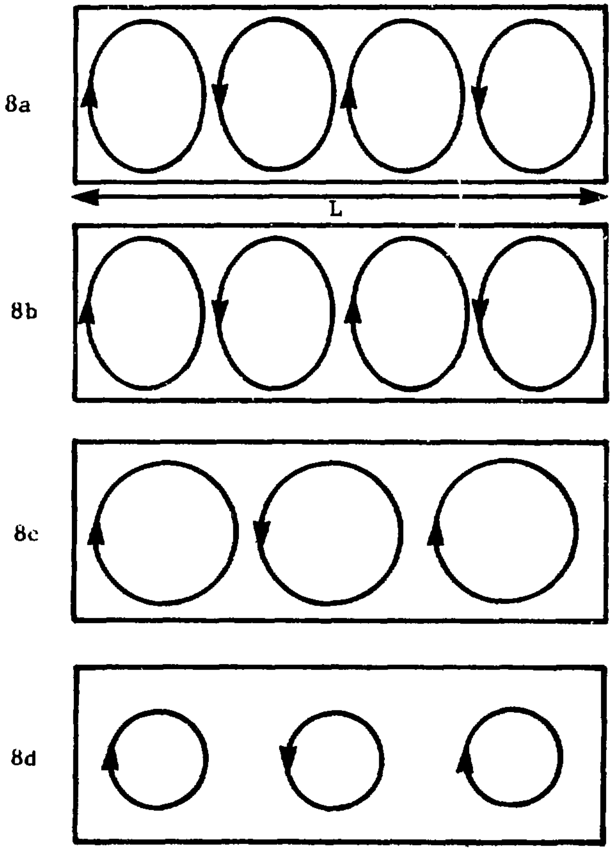

FIGURE 4: Steady Field of the Streamline ($\psi = \pm 1.001 \times 10^{-11}\ m^2/s$) for the simulations 8a to 8d, with Ra* = 108 and F = 3. The rock matrix thickness increases from simulation 8a to 8d passing from 0 to a third of the fissure thickness.

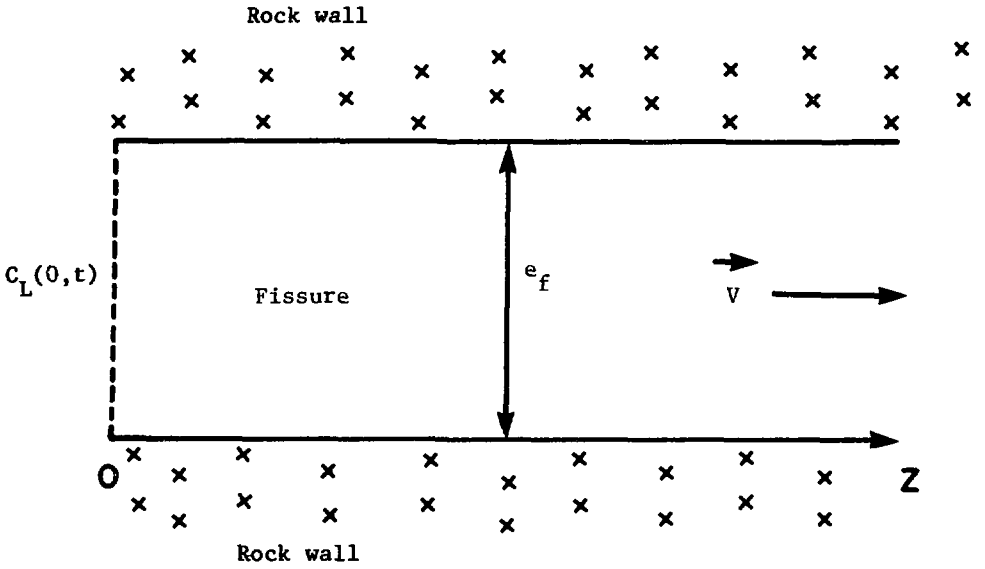

FIGURE 5: Studied Configuration. V: Darcy's flow velocity of the fluid in the fissure, $C_L(o,t)$: imposed concentration at the origin

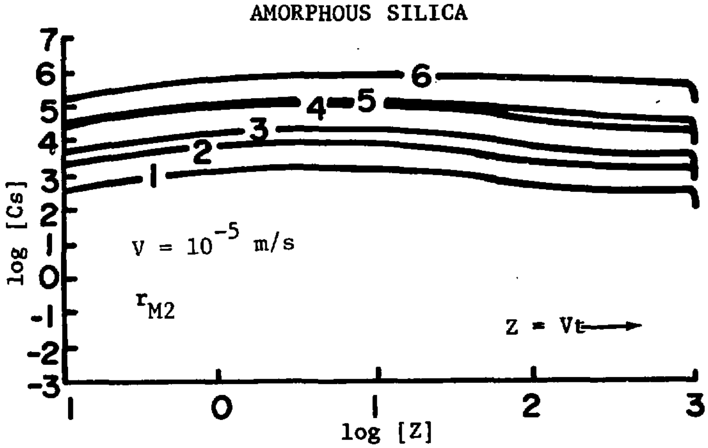

FIGURE 6: Precipitated Mass Per Unit of Fissure Volume (C_s) Versus the Distance from the Waste Disposal to the Surface. V: flow velocity of the fluid in the fissure; r_{M2}: kinetic coefficient ($r_{M2} = 2.5 \times 10^{-5}$ to 2.5×10^{-8} Z by s^{-1}); the curves 1 to 6 correspond to the dates t = 10, 50, 100, 500, 1000 and 10 000 years after the disposal is placed into the massif.

THE GEOCHEMISTRY OF HIGH-LEVEL WASTE DISPOSAL IN GRANITIC ROCK

Bert Allard*

1. INTRODUCTION

The rock groundwater can be considered as a multi-component two-phase system with chemical properties defined by the various solid phases and their interactions with water and dissolved species in the water. Radionuclides from an underground waste repository are eventually released into this system and possibly transported with the flowing groundwater. Here the groundwater plays two roles:

- A chemical buffering agent largely defining the speciation and chemical properties of the dissolved trace radionuclides
- A medium providing transport, also where most of the chemical reactions would occur.

Also, the role of the rock phase is two-fold, in terms of the influence on radionuclide mobility:

- A buffering system that alters and determines the chemical composition of the mobile aqueous phase
- A provider of surfaces that would interact with dissolved species in various ways, leading to a reduced nuclide mobility in most cases.

Any geochemical work within the waste disposal area should evidently aim at

- defining the two-phase systems provided by nature with respect to relevant composition and processes
- defining the chemical behaviour of pertinent radionuclides in these systems.

2. WASTE-FORM LEACHING MODELS

The leaching model for the dissolution of UO_2 proposed by Goodwin agrees quite well with experimental observations (leaching at low pH) and expected behaviour considering the composition of irradiated UO_2. According to this model two different stages can be distinguished:

- Incongruent dissolution; instant release of elements from the fuel sheath gaps; expected for Cs, I and certain activation products.

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* (This paper was submitted at the workshop but B. Allard had to leave before it could be presented.)

- Congruent dissolution; dissolution of the UO_2 matrix, limited by its low solubility.

However, the congruent dissolution phase might in fact turn out to be incongruent as well for the following reasons:

- Although the UO_2 matrix might form a solid solution with the generated fission products and transuranium elements, it is not entirely homogeneous. A variation with depth from the surface is expected, depending on the differences of the conditions in the pellet during irradiation in terms of temperature and neutron flux. It is not known whether this slight inhomogeneity would lead to some incongruence in the dissolution.

- The dissolution might be congruent with respect to some elements (e.g. the actinides) but incongruent with respect to others which might be accumulated on UO_2 grain boundaries.

- The dissolution of the UO_2 matrix would largely be affected by the composition of the water, especially with respect to pH, Eh and complexing agents. Here pH is normally buffered due to the carbonate content and also stabilised in the presence of, for example, a bentonite buffer, and Eh would be buffered by Fe(II) in the backfill (and surrounding rock). However, after a container failure, when the dissolution starts, the change both of pH and Eh (to oxidizing conditions) must be considered even after a long time due to radiolysis. This could lead to the following complicated release scenarium:

- U(IV) is partly oxidized to U(VI); however both Pu and Np could still exist in their lower oxidation states as long as they can interact with U(IV).

- The dissolution of the matrix is limited (in the limited amount of water available) by some other sparingly soluble oxide phase (composition between the two extreme phases $UO_2(S)$ under reducing conditions and UO_2 (OH)2(S) under oxidizing conditions).

- The absolute upper solubility limit would be determined by the amount of complexing agents in the water (diffusion controlled transport from the surroundings to the UO_2-surface), largely $HCO_3^- - CO_3^{2-}$

- Released U(IV) + U(VI) and transuranium elements in lower oxidation states would sorb on the still intact UO_2 matrix, as well as on corrosion products from the canister etc.

The dissolution of the UO_2-pellets as well as the subsequent redox-reactions and sorption phenomena can hardly be modelled from thermodynamic data alone. Therefore two sets of experimental studies would be required.

- Demonstration of the extent of a-radiolysis under proper conditions (e.g. diffusion controlled supply of water, anoxic conditions, contact with a clay buffer, contact with a metal canister that may be oxidized etc). It is not even certain that oxidation of UO_2 will ever occur. No evidence has been found in nature indicating that radiolysis alone would be the cause of uranium oxidation.

- Integrated leaching and migration studies of irradiated fuel and the determination of the simultaneous transport (by diffusion) of released radionuclides into a surrounding backfill.

3. EQUILIBRIUM MODELS - THERMODYNAMIC DATA BASES

The modelling of water-rock interactions constitutes an important step in the understanding and prediction of the chemical properties of the two-phase water-rock system. However, the usually quite imperfect agreement between observations and predictions is disturbing, although reasons for this are obvious, as pointed out by Greenwood (e.g. poor data, missed species, missed compounds, slow kinetics). The refinement of data bases, uses of internal consistent data sets, etc. will not alone give reasonable agreement in systems where highly unsaturated or supersaturated phases appear to exist. The possibility of missed compounds or processes should not be overlooked.

In most granitic groundwater systems one would expect a local equilibrium, not with the major components of the rock like the feldspars, but with the surface coatings of weathering products and precipitates in the immediate contact with the groundwater. The importance of calcite-carbon dioxide equilibria should also be considered, since a continuous supply of CO_2-CO_3^{2-} from shallow waters would change the mass balance. The weathering products are typically layer silicates or silicates with lattice defects, etc., i.e. products with very high cation exchange capacities. Typically, most crystalline silicates would exhibit a cation exchange capacity of less than 10 meq/kg (at pH 7-9), except for most of the phyllo silicates (kaolinite up to ca 50 meq/kg, smectites up to 700-800 meq/kg, etc.) and zeolites (often above 100 meq/kg). Thus, the weathering process would:

- release cations from the crystal lattice
- lead to the formation of products of high cation exchange capacities.

What would govern the observed water composition in terms of cations Na^+, K^+, Ca^{2+}, Mg^{2+}) would consequently not be the concentrations in hypothetical equilibrium with the various solid phases but rather reactions involving exchangeable cations. These reactions would be rapid and kinetically limited only by the transport of dissolved species from the aqueous phase to exchange sites in the solid phases. Thus, all of Na^+, K^+, Ca^{2+}, Mg^{2+}, and indirectly pH - CO_3^{2-}, are linked together due to ion exchange processes. Equilibrium models and calculations based on the stability of various solid phases, etc. can never be expected to describe the conditions in a multi-component system where the fastest chemical reactions would be secondary processes of ion exchange type. These reactions do not appear to be included in any of the major standard codes for rock-water equilibrum calculations.

The purpose of water-rock interaction studies should primarily be the assessment of radionuclide reactions in the water-rock system. Particularly for the actinides, which would largely dominate the biological hazards from spent fuel already after less than 100 years after the discharge from the reactor, it is important to be able to model speciation and solubility, as well as sorption phenomena (see below). Environmental actinides chemistry is largely dominated by:

- hydrolysis reactions
- complexation with "hard" ligands, primarily CO_3^{2-}; (also F^- at high F^- concentrations, and low pH; for the tetravalent state), organic acids of humic and fulvic type (particularly at low pH; for the trivalent state, or in shallow waters with high organic contents), and occasionally PO_4^{3-} and SO_4^{2-}
- redox reactions (for U, Np, Pu)

Most conditions can be modelled in an acceptable way considering only hydrolysis, carbonate complexation and redox reactions. Although the thermodynamic data base has improved substantially over the past few years there are still some large uncertainties in the data for important species and systems. The general principle in modelling of speciation and solubility must be that all species that are likely to exist (due to analogy with similar elements, indications from experiments, from accurate thermodynamic measurements etc.) are included regardless of the fact that corresponding thermodynamic data might be poor or even lacking. This leads to the unfortunate situation where some thermodynamic parameters have to be extrapolated or even estimated; otherwise dominating species might be overlooked and calculated speciation etc., completely erroneous. Some important species where the available thermodynamic data are poor are listed below (for hydroxides and carbonates only; actinides denoted by An)

- $An(OH)_2^+$, $\underline{An(OH)_3}$; data uncertain particularly for $An(OH)_3$, which would dominate in solution at high or intermediate pH in the absence of CO_3^{2-}. Some measurements have been made on Am(III), and one single study of Pu(III) from before 1950 as well as one recent measurement are available; the spread in reported constants is at least two orders of magnitude.
- $An(OH)_3(s)$; experimental data from lanthanide systems, as well as a few total-solubility curves for Am are available.

- $An(OH)_2^{2+}$ - $An(OH)_3^{+}$ - $An(OH)_4$ - $An(OH)_5^{-}$; prior to 1978-79 mostly extrapolated data were available for the 1,3- and 1,4 complexes, based largely on measurements in the U(IV)-system of the 1,1 and 1,5 complexes. Recent measurements of the 1,5 complex for U(IV) indicate a much lower formation constant for this species, as well as for the other hydroxides. The fact that the 1,5 complex has not been identified for Th makes the existence of 1,5 species for the other tetravalent actinides (U, Np and Pu) somewhat speculative. Fairly recent measurements of the 1,1, 1,2, 1,3 and 1,4 Pu-hydroxides are commonly cited. However, there is probably progressive error in the constants due to poor control of the oxidation state (oxidation to Pu(V) possible). Thus, the uncertainty in the formation constant for $An(OH)_4^{-}$ species, which would dominate at intermediate pH, is at least one order of magnitude, probably higher; estimated or extrapolated values might in fact be more accurate than experimentally determined and reported data. The existance of $An(OH)_5$ species, for example, for Pu has to be verified, if this species should be considered in model calculations.

- $AnO_2(s)$; reported solubility products in the literature vary from 10^{-47} to 10^{-63}. The degree of crystallinity evidently has a large influence on the apparent solubility product. Recent measurements on well-defined solids (e.g. $UO_2(s)$) indicate solubility products of 10^{-56} or slightly below. Possibly several orders of magnitude lower values could be assessed for highly crystalline compounds.

- The existance and possible importance of An(III) and An(IV) mixed OH^{-}-CO_3^{2-} complexes are not clear.

- $AnO_2CO_3^{-}$, $AnO_2(CO_3)_2^{3-}$, $AnO_2(CO_3)_3^{5-}$; recent data are available for Np. The reported constants agree fairly well for the 1,1 complex, but the difference is up to 4-5 orders of magnitude for the 1,3 complex, which may dominate under oxic groundwater conditions.

- $An_2(CO_3)_3(s)$; only data extrapolated from lanthanide systems are available.

- $Na_{2x-1}AnO_2(CO_3)_x(s)$; solubility measurements on carbonate complexes, which are likely to be solubility limiting, are in progress.

- $UO_2(CO_3)_3^{4-}$; this species would dominate under oxic conditions in the presence of moderate to high concentrations of carbonate. However, the spread in published formation constants is more than two orders of magnitude. The 1,3 complexes would in fact be predicted to be dominating species in solution, in equilibrium with $UO_2(s)$, even under reducing conditions at high carbonate concentrations using the highest formation constant in the literature (which is also related to the most recent measurement!)

- Solubility-limiting U-phases; at intermediate redox potentials (mildly reducing conditions) solubility limiting phases like U_4O_9(s) U_3O_8(s) $Na_2U_2O_7$(s) etc. would be stable. Thermodynamic data for these phases are usually fairly uncertain.

- Uncertainties in standard potentials are usually of the order 50 mV, not due to unprecise measurements but due to difficulties in the assessment of activity factors. Especially for the U(V) - U(VI) and Pu(V) - Pu(IV) systems these uncertainties lead to difficulties in predicting probable oxidation states. Recently published measurements on Pu-oxidation states under oxic conditions can hardly be explained unless the appropriate standard potential is adjusted (within the uncertainty limit) or a correction of the measured redox potential in the system is introduced. The mere fact that seasonal variations of the Pu oxidation state are observed in nature illustrates the necessity of having accurate standard potentials as well as formation constants for the species involved in these equilibria.

- Information on the kinetics, e.g. for redox reactions, but particularly for the dehydration of tetravalent hydroxides, $Au(OH)_4$(s) AnO_2(s), is lacking.

The potentially important organic complexes involving macromolecular natural carboxylic acids should also be emphasised. Information on such complexes, as well as on the properties of the corresponding organic acids from deep groundwaters, is scarce. Generally, there are no methods available for direct studies of the chemical composition of actinides at trace levels (below 10^{-9} M*), at least not on a routine basis.

4. ROLE OF COLLOIDS

The transport of matter in colloidal state is important for many substances and trace elements in nature and must be considered also for radionuclides. Various categories of colloidal particles can be distinguished based on size, charge, stability, composition, etc. One somewhat arbitrary but practical division into various groups may be

- pseudo colloids
- true colloids

Pseudo colloids are particulate aggregates of clay, silica, glass, soil, hydroxides, etc. onto which the trace elements have been sorbed. Naturally, these colloidal particles would be very little affected

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* M = mol/L

by the presence of sorbed trace elements. The mere fact that these colloidal "carriers" exist under certain conditions indicates that they would not be primarily expected to interact with exposed solid surfaces. Undoubtedly pseudo colloids play an important, and perhaps dominating role in the transport of actinides in their lower oxidation states under conditions where open channels are available for water flow. These colloids would, however, be filtered, when passing partly filled channels. For example, they would not diffuse through a clayish layer, and the sorption of the trace element would probably be reversible. Thus, when exposed to "fresh" surfaces a desorption-sorption process of the trace element would be possible. Very little experimental data concerning the mobility of pseudo colloids are available and proper experiments should be designed for this purpose. Especially integrated experiments such as

- dissolution - nuclide transport in glass or vitrified waste systems
- dissolution - nuclide transport in UO_2 systems
- passage through a clay backfill and into a surrounding rock system

must be performed, as well as studies of the predicted reversibility of the pseudo colloid formation.

Two types of "true" colloids can be distinguished:

- thermodynamically stable colloids
- metastable colloids

The thermodynamically stable colloids would constitute chemically stable compounds, such as macromolecular complexes, and polymeric hydroxides in the low pH-range (e.g. Pu(IV)). These species carry net charges and would interact with solid surfaces in various ways. The transport properties of macromolecular organic species require further experimental studies.

Metastable colloidal species would constitute aggregates formed in the course of precipitation or coagulation. Although they do not represent thermodynamically stable species they could exist for a long time due to coulombic repulsive forces. The formation of a neutral (or anionic) hydroxide and the subsequent formation and, with time, crystallisation of tri- and tetravalent actinide hydroxides could lead to an intermediate formation of metastable colloidal species. These species seem to sorb in a way similar to hydrolysed species in true solution, i.e. with a maximum at the pH where neutral species dominate, and with a reduced sorption for anionic species. The formation of true colloids is not likely to constitute any important mobilising factor.

5. SORPTION PHENOMENA

Sorption of trace elements has been studied for various reasons since at least the 20's and 30's (natural radioactive decay products) and more systematically within national waste programmes since the early 70's. Despite the controversy concerning the K_d concept and its usefulness, it is largely possible to assess data for the quantitative interaction between dissolved trace elements and geologic materials with acceptable accuracy (in comparison with all other uncertainties going into any transport model in a geologic system).

Various sorption mechanisms have been identified, and somewhat arbitrarily divided into the following types:

- electrostatic interactions - ion exchange
- physical adsorption
- chemisorption

It should be recognised that other divisions into process types can be made, and that the observed sorption behaviour usually is the sum of several processes.

Laboratory studies of sorption behaviour may be justified for the study of

- sorption mechanisms - e.g. affects of complexing agents
- temperature effects
- reversibility - e.g. for pseudo colloids
- new element systems (protactinium ?)

Also efforts should be made to adjust the enormous amounts of sorption data in the literature to the existing sorption models (or models currently under development), which would require additional information, both on chemical speciation of the radionuclide in the aqueous phase as well as on various parameters of the sorbent. The possibility of predicting or calculating sorption equilibria in simple systems appears to be within reach already with existing models. There will certainly be a need in the future for "best estimate" data based on distribution functions or sorption process model calculations and not merely conservative single values for the safety assessments of waste storage concepts. Also this is within reach, at least in terms of semi-empirical equations that include the effects of major chemical parameters of importance.

Integrated dynamic studies will be required for the modelling of radionuclide transport from a waste repository of

- uptake of radionuclides on a rock surface and penetration into the bulk rock
- barrier effects of fissure coating materials
- availability of microfissures and rock porosity for sorption
- transport under flow conditions in well-defined pathways (fractured or porous media)
- large-scale and in-situ tests
- verification from natural analogs

The verification under field conditions of results and predictions from laboratory measurements must be considered as an extremely important task with high priority.

WORKSHOP PROGRAMME

MONDAY, SEPTEMBER 12TH

1500 onwards	Arrival and Registration
2000 - 2045	Welcome and Introductory Talk by Dr. F. Girardi, CEC Research Establishment, Ispra, Italy.

TUESDAY, SEPTMEBER 13TH

0845 - 1045	SESSION ONE: Discussion leader Dr. B.W. Goodwin, AECL Whiteshell. "Validity of long-term waste form leaching models"
1100 - 1300	SESSION TWO: Discussion leader Dr. B. Skytte Jensen, Riso, Denmark. "Applicability of equilibrium models, kinetic data, and use of low temperature experimental data"
1500 - 1800	Group Discussions
2000 - 2200	SESSION THREE: Discussion leader Dr. H.J. Greenwood, University of British Columbia, Canada, "Thermodynamic data bases and geochemical models"

WEDNESDAY, SEPTEMBER 14TH

0845 - 1045	SESSION FOUR: Discussion leader Dr. A. Avogardro, CEC Research Establishment, Ispra, Italy. "Role of colloids and filtration"
1100 - 1300	SESSION FIVE: Discussion leader Dr. I.G. McKinley, EIR, Zurich, Switzerland. "Applying complex sorption data to transport models: simplifying sorption parameters"
1500 - 1700	Group discussions

THURSDAY, SEPTEMBER 15TH

0845 - 1045	SESSION SIX: Discussion leader Dr. F.J. Pearson, INTERA, Houston, USA "Linking flow and geochemical models: fully coupled models"

1100 - 1300	SESSION SEVEN: Discussion leader Dr. J.F. Barker, University of Waterloo, Canada "Microbiological aspects and redox potential in nuclide release and migration"
1500 - 1800	Group discussions
2100 - 2200	OPEN SESSION (Short discussion papers)

FRIDAY, SEPTEMBER 16TH

0930 - 1130	CLOSING DISCUSSION: Chairmen Dr.N.A. Chapman, ISMES, Rome, Italy Dr. F.P. Sargent, AECL, Whiteshell, Canada.
1315	Bus departs for Heathrow airport

PARTICIPANTS

Dr. B. Allard
Dept. of Nuclear Chemistry
Chalmers Institute of Technology
S-412 96
Goteborg, Sweden

Dr. M. Apted
Rockwell Hanford Operations
Richland, Washington
U.S.A.

Dr. A. Avogadro
CEC Chemical Division
Joint Research Centre
Ispra (Varese)
Italy

Dr. J.F. Barker
Dept. of Earth Sciences
University of Waterloo
Waterloo, Ontario
Canada
N2L 3G1

Dr. G. Bidoglio
CEC Chemical Division
Joint Research Centre
Ispra (Varese)
Italy

Dr. T.H. Brown
Dept. of Geological Sciences
University of British Columbia
Vancouver, B.C.
Canada
V6T 1W5

Dr. N.A. Chapman
ISMES
Via Torquato Taramelli
1400197 Rome
Italy

Dr. N. Christofi
Dept. of Biological Sciences
Napier College
Edinburgh, Scotland

Mr. Bernard Come
CEC
200 Rue de la Loi
Room SDM 1/76
1049 Brussels
Belgium

Dr. G. de Marsily
École Nationale, Supérieure Des Mines
Centre D'Informatique Géologique
35, Rue Saint-Honoré
77305 Fontainebleau
France

Dr. W.S. Fyfe
Dept. of Geology
University of Western Ontario
London, Ontario
Canada
N6A 5B7

Dr. F. Girardi
CEC
Joint Research Centre
21020 ISPRA (Va)
Italy

Dr. B.W. Goodwin
Environmental and Safety
Assessment Branch,
Atomic Energy of Canada Limited,
Whiteshell Nuclear Research Establishment,
Pinawa, Manitoba
Canada
ROE 1LO

Dr. H.J. Greenwood
Dept. of Geological Sciences
University of British Columbia
Vancouver, B.C.
Canada
V6T 1W5

Dr. Bror Skytte Jensen
Chemistry Dept
Riso National Laboratory
DK - 4000 Roskilde
Denmark

Dr. F. Lanza
CEC Chemical Division
Joint Research Centre
Ispra (Varese)
Italy

Dr. I.G. McKinley
Gastehaus NR 4 Bein Walk
EIR
CH 5303
Wurenlingen, Switzerland

Dr. T.W. Melnyk
Geochemistry & Applied
Chemistry Branch,
Atomic Energy of Canada
Limited,
Whiteshell Nuclear Research
Establishment,
Pinawa, Manitoba
Canada
ROE 1LO

Dr. J.B. Moody,
ONWI
Battelle Memorial Institute
505 King Avenue
Columbus, Ohio
U.S.A. 54201

Dr. F.J. Pearson
Intera Env. Cons. Inc.
11999 Katy Freeway Suite 610
Houston, Texas
U.S.A. 77079

Dr. D.L. Rancon
Département De Sûreté Nucléaire
SRS-SESTR
C E N De Cadarache
B P No 1, 13115
St. Paul-Lez-Durance
France

Dr. A. Saltelli
CEC Chemical Division
Joint Research Centre
Ispra (Varese)
Italy

Dr. F.P. Sargent
Chemistry & Applied
Chemistry Branch,
Atomic Energy of Canada
Limited,
Whiteshell Nuclear Research
Establishment,
Pinawa, Manitoba
Canada
ROE 1LO

Dr. David Savage
Fluid Processes Research Group
British Geological Survey
Keyworth
Nottingham, U.K.

Dr. G.B. Skippen
Dean of Science
Carelton University
Ottawa, Ontario
Canada

Mrs. J.M. West
Fluid Processes Research Group
British Geological Survey
Keyworth
Nottingham, U.K.

Dr. T.J. Wolery
Lawrence Livermore Laboratories
University of California, P.O. Box 808
Livermore, California
U.S.A. 94550

OBSERVERS

Dr. J.O. Duguid
Battelle Project Management Division
2030 M St. N.W.
Washington, D.C.
U.S.A. 20036

Dr. E.S. Patera, Geochemist
Crystalline Rock Project Office
Department of Energy
Chicago Operations Office
9800 South Cass Avenue
Argonne, Illinois
U.S.A. 60439

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