

FOREIGN TRIP REPORT

Project MIRAGE - Second Phase - Plenary Meeting
Commission of the European Communities (CEC)
R&D Programme: Management and Storage of
Radioactive Waste

Brussels, Belgium
March 16 - 17, 1989

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12 April 1989

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PACIFIC NORTHWEST LABORATORY
Richland, Washington 99352

Operated for the U.S. Department of Energy by
Battelle Memorial Institute
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SUMMARY

DATE OF REPORT April 12, 1989

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DESTINATION Project MIRAGE - Second Phase Plenary Meeting
Commission of the European Communities (CEC)
Brussels, Belgium

PURPOSE OF THE TRIP The traveler attended the CEC's MIRAGE Project meeting as an observer representing the Office of Civilian Radioactive Waste Management, U.S. Department of Energy, Washington, D.C.

REPORT ABSTRACT Progress was reviewed in four major research areas pertaining to the Migration of Radionuclides in the Geosphere (MIRAGE). MIRAGE Project work is addressing problems that are potentially of interest to both the OCRWM and Defense Programs divisions of the Department of Energy. Radionuclide migration is a problem being modelled in assessments of performance of high-level, low-level, and transuranic waste disposal facilities. The four research areas reviewed presented at this MIRAGE meeting included: 1) Geochemistry of Actinides and Fission Products, 2) Calculation Tools, 3) In-Situ Experiments, and 4) Natural Analogues. MIRAGE Project research addresses the needs of national programs evaluating potential sites in geologic settings not readily comparable with the unsaturated tufaceous rock setting being addressed by the U.S. high-level waste program. Thus the potential usefulness of MIRAGE results in the high-level waste program lies in the area of laboratory and field experimental and analytical technique development, as well as in advances in numerical methods and computer codes. The work being done in MIRAGE to generate and evaluate thermodynamic data also seems likely to be of interest to the U.S. high-level waste program. Transuranic and low-level waste programs may be able to directly benefit from MIRAGE work addressing radionuclide behavior in a variety of natural systems, and complete drafts of the presentation materials are attached for study by interested parties representing those programs.

COST OF TRAVEL \$ 1080.17 travel costs, \$ 2660 labor costs, U.S. Department of Energy contract DE-AC06-76RLO 1830.

DETAILED TRIP REPORT

PURPOSE

The traveler's purpose was to observe the second plenary meeting of the CEC's MIRAGE Project on behalf of the U.S. Department of Energy's Office of Civilian Radioactive Waste Management. The OCRWM was invited to send an observer to this meeting by the CEC in accordance with the provisions of an existing cooperative agreement.

IMPORTANCE OF MIRAGE TO OCRWM AND OTHER DOE PROGRAMS

The Migration of Radionuclides in the GEosphere (MIRAGE) Project is concerned with defining the scientific basis of radionuclide behavior in the geosphere. Thus, the MIRAGE Project mission corresponds to the mission of the OCRWM's Yucca Mountain Project's Geochemistry Program, as described in the Yucca Mountain Project Site Characterization Plan. In particular, Table 1 presents a listing of some of the topical materials currently being considered for the Safety Analysis Report (SAR) that is to be part of the License Application, and a listing of the research topics being addressed by MIRAGE. Table 1 only shows a selected number of subtopics being considered by the Yucca Mountain Project Geochemistry Program under the general topic of Radionuclide Retardation Properties.

Table 1 shows that similar work is being planned or performed for the MIRAGE Project and the OCRWM's Yucca Mountain Project. This does not suggest, however, that what is done for MIRAGE may be used to address radionuclide transport issues for the Yucca Mountain Project site. The combinations of geochemical and physical processes expected to define radionuclide migration behavior in the Yucca Mountain's unsaturated environment are not necessarily comparable with those operative in the clays, sediments, and granites being addressed in MIRAGE work. Thus, much of MIRAGE's site-specific and laboratory work using site-specific materials will not be directly usable by the Yucca Mountain Project of OCRWM.

Some of the downhole characterization technology being developed under the auspices of MIRAGE would have limited usefulness to the Yucca Mountain Project because it is designed for testing the properties of - and radionuclide behaviors in - saturated environments. Nevertheless, these techniques may be of interest to Yucca Mountain Project studies that are to define transport properties in the saturated tuffs and sediments at some distance from the repository, the far field. MIRAGE experience in the development and comparison of techniques for characterizing naturally occurring particulates, colloids, and natural organics may be directly useful to the Yucca Mountain Project.

Similarly, thermodynamic data on colloid-formation, speciation and complexation developed under MIRAGE should be directly useful to anyone concerned with modeling radionuclide behavior in the geosphere. For example, the DOE Defense Programs' low-level waste functions must model radionuclide migration in the presence of humic acids and, perhaps, carbonate-bearing waters. MIRAGE work in quantifying the effects of natural organics and carbonates on transport may thus be directly useful in low-level waste system performance assessment.

The clay-site work and much of the natural analog work being carried out under MIRAGE may also be of interest to the Defense Programs' low-level waste system performance effort. Radionuclide interactions with clays, and the hydraulic properties of clays, would be of interest in systems where clay liners are employed, for example. On the other hand, some of the work directed at defining methods for the characterization of clays and sediments, particularly with respect to identifying the properties important to transport, could be of interest to the Yucca Mountain Project.

Finally, selected portions of the modeling being done for MIRAGE closely parallel that being done for the Yucca Mountain site, particularly the sorption, colloidal transport, speciation and solubility modeling. The comparison of geochemical models in an international benchmarking exercise (CHEMVAL) may provide information on model database adequacy by testing models in geochemically different environments wherein the solid phases controlling an element's solubility may differ significantly.

Table 1. Topics of Interest to the OCRWM's Yucca Mountain Project, and MIRAGE Project Research Areas.

TOPICS OF INTEREST TO OCRWM	MIRAGE RESEARCH AREAS
1. SOLUBILITY (Research & Modeling): <ul style="list-style-type: none"> • Speciation & Complexation • Actinide Colloid Formation • Solubility Calculations • Solubility Determinations 	1. SOLUBILITY: <ul style="list-style-type: none"> • Actinide Speciation & Complexation Measurement • Solubility Measurement & Modeling
2. SORPTION (Research & Modeling): <ul style="list-style-type: none"> • Actinide Batch Sorption • Sorption Isotherm Deconvolution • Ground-Water Composition & Sorption • Sorption on Particulates • Microbial & Colloid Transport 	2. SORPTION: <ul style="list-style-type: none"> • Investigations of Basic Retention Mechanisms • Ground Water Composition Affects • Organics and Colloids • Thermodynamic Data
3. GEOCHEMICAL/GEOPHYSICAL MODEL: <ul style="list-style-type: none"> • Geochemistry Field & Lab Tests • Natural & Anthropogenic Analogs • Modeling of Transport • Transport Process Significance 	3. MODELING: <ul style="list-style-type: none"> • Field and Lab Studies • Natural Analog Studies • Transport Modeling • Coupled-Effects Studies
4. GEOCHEMICAL CHARACTERIZATION: <ul style="list-style-type: none"> • Pathways Characterization • Mineralogic Characterization • History of Chemical Alteration 	4. CHARACTERIZATION: <ul style="list-style-type: none"> • Development of Characterization Tools and Procedures • Characterization of Natural Aquifers & Groundwaters

DIGEST OF MEETING ACTIVITIES

ATTENDEES

Attendees represented CEC member nations participating in the MIRAGE Project and invited observers. No attendance list was made available at or following the meeting.

AGENDA

The Programme handed out at the meeting is Attachment 1. The meeting consisted of overview papers being presented that addressed the MIRAGE Project's four major research areas:

- Geochemistry of Actinides and Fission Products
- Calculation Tools
- In - Situ Experiments, and
- Natural Analogues.

TRAVELER'S ROLE

The traveler's role was to observe this meeting of the CEC's MIRAGE Project on behalf of the DOE Office of Civilian Radioactive Waste Management. The traveler was not invited to speak or formally contribute to the meeting. The traveler took part in the question and answer sessions which were open to all attendees.

DESCRIPTION OF MEETING

The four Programme divisions (Attachment 1) listed under AGENDA, above, are used in this meeting description. Introductory remarks by Piere Venét and Bernard Côme gave an overview of 1988 progress in MIRAGE and explained the ground rules for this meeting.

Research Area: GEOCHEMISTRY OF ACTINIDES AND FISSION PRODUCTS

An introductory speaker, I. M. Ginniff of the U.K., noted that actinide chemistry was important in terms of the near field and the far field repository issues because actinides were a large part of the inventory and actinide behavior was important to repository design and site selection. The year 2005 was given as the time a repository would be functioning in the U.K., but already questions were being asked as to what may be included in the waste stream and what must be excluded. The work on actinide-organic interactions, being sponsored by MIRAGE, was of particular importance in this respect, since the use of organics in reprocessing creates organic waste that may or may not be treated prior to disposal. Trace organics in the waste were, perhaps, unavoidable and thus their potential role in actinide transport must be quantitatively addressed. The need for applicable natural analogs to give confidence to the ability to predict long-term in-situ behavior was mentioned.

Summary Overview of the Research Area

The summary overview of progress in this Research Area is attached (Attachment 2). This Research Area covered three efforts: 1) actinide complexation with humic acids; 2) colloid generation; and 3) evaluation of retention mechanisms. In addition, some experimental work is aimed at defining thermodynamic data values needed for other MIRAGE activities.

Humic acid complexation Of interest to all organizations concerned with geosphere disposal of chemical and radioactive wastes is the characterization of potentially complexing natural organics such as the humic and fulvic acids. Fulvic acids are yet to be addressed by MIRAGE, and completed and current work has concentrated on the description of humic acids in terms meaningful to migration modeling. In terms of preliminary results, the size of the humic acid particle appears to be important to migration modeling, and size is a function of ionic strength, pH, and co-solute cations. Experience with the characterization of humic acids, resulting from interlaboratory comparisons, is discussed in Attachment 2, and should be of interest to the Yucca Mountain Project since humic acids in potential migration pathways are to be characterized.

An interlaboratory comparison of radionuclide/humate complexation behavior resulted in some preliminary estimates of complexation constants. The interpretation of data relies on the use of mathematical fitting techniques and does not reflect a mechanistic understanding of complexation between multivalent cations and polyelectrolyte ligands. Basic research is needed to allow the formulation and testing of mechanistic complexation hypotheses.

Colloid generation As in the case of evaluating humic acid interactions with radionuclides, the evaluation of the importance of colloids in migration requires the characterization of naturally occurring and radionuclide colloids. Thus, research under this heading is concerned with defining colloids quantitatively, and this is being addressed through a series of interlaboratory, characterization attempts. The preliminary results of MIRAGE efforts include the realization that a new method is needed for colloid population and size distribution determinations.

The generation of transuranic radionuclide colloids as well as naturally occurring true- and pseudo-colloids is under investigation. No preliminary results are reportable at this time.

Retention mechanisms Work has only recently begun in this area and preliminary conclusions are not particularly noteworthy at this point in time. Experience is being gained in the detection of speciation products using a variety of measuring techniques. This aspect of the work under this heading may be of immediate interest to experimental geochemists and chemists charged with supporting the use of equilibrium speciation calculations for a specific element at a specific site.

Database support Activities under this heading include the evaluation of experimental data currently available. Problem areas uncovered so far include

the lack of data for organic complexation and the contradictions in constants available for actinide hydrolysis and carbonate complexation.

Grimsel Colloid Benchmark Status-Report

The Grimsel rock laboratory in Switzerland has been equipped with a flow-through system that allows sampling of groundwater inside a granite mountain. The samples are sampled and distributed to four laboratories under anaerobic conditions. The four laboratories anaerobically separate and concentrate the samples and distribute them to 12 participating analytical laboratories. The results of this intercomparison are to be reported in 1990.

Problems that have been identified at this stage include those to be expected when working with samples from a reduced, anaerobic environment. Air contamination drops the pH of the water from 9.6 to 8, with corresponding changes in the redox state and chemistry.

Colloid characterization has emphasized the determination of size distributions, but chemical characterizations have also been done. The separation and storage processes seem to introduce problems mostly relatable to air contamination. Filtration for particle size distribution profile characterization seems to interfere with the characterization of the filtrate's solution chemistry which must be known to understand colloid-solution chemistry interactions. Salt retention by filters at the 2.1 to 1.5 nm level seems to introduce anomalies in the solution chemistry.

Research Area: CALCULATION TOOLS

The MIRAGE Project's calculation tools research area consists of a multitude of contracts dealing in code development, verification, and validation. The summary overview (Attachment 3) gives a short description of work in each contract, except for the CHEMVAL exercise and work on uncertainty analysis methods, which were covered in separate presentations (see below). One of the MIRAGE contracts explicitly covers participation in HYDROCOIN and INTRAVAL, the hydrologic and transport code verification and model validation exercises of the Swedish Nuclear Power Inspectorate and the OECD/NEA (See part 2.1.4 [ii] of Attachment 3).

Summary Overview of the Research Area

The summary overview of progress in this Research Area is attached (Attachment 3). A table summarizing the wide range of research activities described in this attachment has been prepared for the convenience of the reader of this report. Table 2 gives the section number and title of the work as it appears in Attachment 3, a few lines describing the work, and a cursory description of any plans for continuing work or of conclusions discussed in Attachment 3. All of the work described in Attachment 3 is ongoing, and it should be remembered that all conclusions are preliminary. Activities that, in the opinion of the traveler, may be of particular interest to Yucca Mountain Project modelers, are 2.1.1, 2.2.1, 2.2.2, 2.2.3, and 2.2.5.

Table 2. Status of Model Application (2.1) and Model Development (2.2) Activities Under the Calculation Tools Research Area of the CEC's MIRAGE Project (Numbers keyed to Attachment 3) (Part 1 of 5)

Activity #	Activity Title	Purpose, Status and Planned Work	Preliminary Conclusions or Problems
2.1.1	Interpretation of in situ tracer tests at Driggs, U.K.	To understand & compare meter-scale tracer tests in a homogeneous sandy aquifer and validate a modelling concept for small-scale heterogeneities. Two conservative-tracer tests have been carried out and modeling has been done to interpret the experiments. Mildly sorbing tracers are to be used next, and modeling is to use batch and column K_d 's.	Parallel flow fields were found between the injection and sampling piezometers, and this allowed vertical permeability distributions to be calculated. The problem is that these calculated properties do not match those measured in slug tests performed with special equipment that measured permeabilities at 0.2 m intervals. The measured permeabilities were used to model breakthrough times and the match with observed times were not good. Thus, there are problems in measuring permeabilities even in a well-known medium at the meter scale which is related to the question of how to define an acceptable degree of uncertainty, and calls into question the attempt to estimate ground water travel times. (See the writeup in Attachment 3).
2.1.2	Geochemical modeling in France	Crushed limestone columns with clay impurities were injected with $SrCl_2$ at various temperature and concentration levels. Breakthrough results were modeled using a coupled model that included a number of phenomena. This was to be a validation exercise, but both the experiment and the modeling proved difficult.	The fit between calculated and observed strontium and chloride breakthrough curves was unsatisfactory. Explanations included unexplained observed phenomena and the inability of the modeling to handle significant clay-sorption. The experiments and models need improving, but the present results do seem to call into question the wisdom of the trend toward ever more complex models.

Table 2. Status of Model Application (2.1) and Model Development (2.2) Activities Under the Calculation Tools Research Area of the CEC's MIRAGE Project (Numbers keyed to Attachment 3) (Part 2 of 5)

Activity #	Activity Title	Purpose, Status and Planned Work	Preliminary Conclusions or Problems
2.1.3	Thermo-hydro-mechanical modeling in France	This is a modeling exercise addressing the changes in hydraulic behavior in a granite block due to heat loading, thermal stress relief, and buoyancy. Preliminary modeling has been done taking into account pressure gradients and buoyancy. Later calculations will include changes in permeability over time. A validation large scale block test is also planned.	Large porosity increases were calculated in response to the thermal stresses and fracture-responses assumed and modeled. These results represent a preliminary sensitivity study, however, and must be put into perspective as part of a total system performance assessment.
2.1.4 (i)	Flow and transport calculations in the Netherlands (i): the generic safety assessment	The generic safety assessment addressed the safety of deep-borehole and mined high-level waste repository systems in domed and bedded salt formations. The time period considered was 10 ⁵ years, thus, many scenarios, including several geodynamic scenarios were considered. Publication in 1990.	The source term modeled in this safety assessment is an accidental water intrusion that results in the expulsion of materials through a fracture or backfilled galleries. This is not a likely scenario, but does allow an evaluation of a failed containment system. This work may be of interest to modelers at the Waste Isolation Pilot Plant.
2.1.4 (ii)	Flow and transport calculations in the Netherlands (ii): METROPOL validation	The METROPOL code is being used to model several HYDROCOIN and INTRAVAL problems. In addition, as part of the PAGIS exercise, METROPOL was used to model the Gorleben, F.R.G. region and the results compared with results using the SWIFT code.	Density variations have been difficult to model. Large scale modeling has required fine computational meshes that make SWIFT very expensive to run. Thermal density change experiments were found to be inadequate for validating brine density problem calculations. Validation attempts so far have been less than convincing.

Table 2. Status of Model Application (2.1) and Model Development (2.2) Activities Under the Calculation Tools Research Area of the CEC's MIRAGE Project (Numbers keyed to Attachment 3) (Part 3 of 5)

Activity #	Activity Title	Purpose, Status and Planned Work	Preliminary Conclusions or Problems
2.1.4 (iii)	Flow and transport calculations in the Netherlands (iii): brine flow experiments	Laboratory experiments using fresh water and brine are addressing the possible need for including generally neglected terms in the formulations of Darcy's and Fick's laws. Experiments performed thus far have been inconclusive and further work is planned.	The changes observed in the experiments are encouraging in that they suggest the modified models may represent an improvement, but this improvement is so small as to be of doubtful significance, and the work should continue.
2.1.4 (iv)	Flow and transport calculations in the Netherlands (iv): METROPOL improvements	A number of improvements have been included in METROPOL this year, and a number of others are ongoing. This model development activity is being conducted in parallel with the model-application activities described above.	Temperature effects on transport and a probabilistic capability are part of a longer list of enhancements being made to METROPOL.
2.1.5	Modeling at Mol, Belgium	Regional modeling of flow through the Boom clay formation, as well as laboratory and in-situ experiments on radionuclide migration in clay plugs, are part of the modeling at Mol. The regional modeling is using updated clay pore-water ages as a partial check on the validity of the measured porosities used in modeling.	It is hoped that improved ages for the clay pore-waters will help the evaluate the calculated leakage flux-through the clay formation. The clay plug experiments have resulted in good agreement between experiment and modeling, at this small scale. In addition, results call into question the need to invoke the new concept of 'surface diffusion.' By using radionuclide-specific accessible porosities, the experimental results are interpretable.

Table 2. Status of Model Application (2.1) and Model Development (2.2) Activities Under the Calculation Tools Research Area of the CEC's MIRAGE Project (Numbers keyed to Attachment 3) (Part 4 of 5)

Activity #	Activity Title	Purpose, Status and Planned Work	Preliminary Conclusions or Problems
2.2.1	Geochemical modeling at RISO, Denmark	The WHATIF code series (WHATIF-AQ is the equivalent of EQ3; WHATIF-PW is equivalent to EQ6) is being improved. A TURBO-PASCAL WHATIF-AQ now runs 50 times faster than the BASIC version, PW conversion is to follow. Stochastic capabilities are being developed, and database development is also being pursued.	To address the well-known problem of the predicted solid phases not being observed, a kinetic capability is being developed to help predict the likelihood of mineral formation. Although clay-surface ion-exchange is included, the capability to model other surface types is being addressed. The WHATIF and EQ code series are being used in the CHEMVAL benchmarking exercise discussed elsewhere in this report.
2.2.2	Geochemical modeling work at the British Geological Survey	The BGS work involves batch, diffusion and column experiments to study transport of the Co-EDTA complex. Further work is directed at adding a cation/organic-macromolecule interaction capability to the PHREEQE code.	Stability and dissociation data is being obtained experimentally. PHREEQE enhancements involve a discrete ligand model including electrostatic surface interactions, but surface complexation and empirical titration-curve models are also being considered.
2.2.3	Model development at Harwell, U.K.	This work is in progress and is aimed at 1) Improving methods for solving non-linear problems, 2) Incorporating chemical reactions into a transport code previously only using K_d s, 3) Creating a model for the advance of a sharp front, 4) Using a stochastic, 3-dimensional model to analyze solute transport in heterogeneous porous media, and 5) Modeling fracture network transport.	The activity addressing solute transport in heterogeneous media on the meter scale, is discussed in terms of preliminary conclusions about the calculations and results. The time-intensive stochastic approach seems more necessary for early times, while the computationally more efficient deterministic approach seems usable at larger times and distances. The scaling problem is being addressed.

Table 2. Status of Model Application (2.1) and Model Development (2.2) Activities Under the Calculation Tools Research Area of the CEC's MIRAGE Project (Numbers keyed to Attachment 3) (Part 5 of 5)

Activity #	Activity Title	Purpose, Status and Planned Work	Preliminary Conclusions or Problems
2.2.4	Non-dominant thermodynamic processes at CEA-EMP in France	This ongoing work addresses the role of non-dominant thermodynamic processes in transport of radionuclides away from a repository. The processes being investigated include thermally induced diffusion and thermogravitation (a buoyancy-induced convective cell in a fracture). Modeling is complemented by experimental work designed to validate aspects of the modeling.	The attempts to validate the modeling of these effects through detailed experiments on homogeneous sand columns have not been without problems, and new experiments are being carried out. The fracture convection cell has been modeled, but is not being addressed experimentally. Additional non-dominant effects are being addressed as this work continues.
2.2.5	Development of CHEMTARD simulation	The CHEMTRN code developed at Lawrence Berkeley Laboratory has been significantly modified and enhanced, and is now called CHEMTARD. It is either a stand-alone coupled-transport model or can be used as an integral part of a system of codes for repository safety assessments.	There is no description of this work in Attachment 3. No discussion was scheduled due to time constraints. Interested parties may contact the principal investigators, D. Read or S. K. Liew of W.S. Atkins Engineering Sciences, Epsom, U.K.
2.2.6	Fuzzy set theory	A presentation of this work was given, addressing alternative approaches for treating uncertainty in modeling. This presentation by W. Shaw of the U.K. was a tutorial on fuzzy set theory and explained how this theory could be used to model uncertainties in differential equations.	This presentation seemed to suggest that the fuzzy sets approach, which required the propagation of ranges rather than point values through calculations, fell somewhere between a deterministic and a stochastic approach. In the question period the presenter seemed to agree that if data were available to support the use of a stochastic approach, then the fuzzy set approach would not be very useful.

The CHEMVAL Exercise

A separate report was given on progress in CHEMVAL. The report is included as Attachment 4.

CHEMVAL is a three stage exercise: 1) benchmarking of speciation codes, 2) validation of speciation models with experimental data, 3) verification of coupled transport codes, 4) validation of coupled models against experimental data. The success of CHEMVAL is important in terms of the overall credibility it can potentially lend to geochemical and transport modeling in general. What may be particularly important for OCRWM, however, is the participation of a group using the EQ3/EQ6 set of codes, the same codes that are being used within the Yucca Mountain Project. To support CHEMVAL, a database-definition effort is also underway.

The first stage benchmarking exercise underscored the importance of the database used in a code. The participating codes were found to be capable of solving the range of geochemical problems posed, but shortcomings were identified for each code (a reference [5] is given in Attachment 4, but was not available at the meeting). A specific set of database shortcomings was identified [See Table II of Attachment 4] that may be of interest to the Yucca Mountain Project.

The second stage of CHEMVAL involves modeling four ground waters and experiments:

- Mol, Belgium, ground water in organic-rich clay
- Gorleben, F.R.G., actinide solubility trials in ground waters from the water-bearing strata above a potential salt repository
- Maxey Flats, Kentucky, waters from an existing low level waste facility
- Oman, highly alkaline spring waters thought to be comparable with cement waste-form pore waters

The presentation focused on the Mol and Gorleben preliminary results. A synthetic Mol clay water was made and the solubility of Am, Np, and Pu were predicted reasonably well and to be constrained by the solid phases found in the experiment. Although this is good, the actual Mol ground water has a considerable organic loading and the models are not capable of predicting organic complexation.

In the brackish Gorleben waters, the presence of organic and inorganic colloids presented problems. When 1 nm filtrates were used predictions matched experimental Am solubilities well, but when 450 nm filtrates were used there were greater discrepancies. The overpredicting of Am concentrations in the coarser filtrate is explained by elevated analyses of potential complexing ligands that would keep Am in solution, which are included in the model, and the presence of sorbing colloidal materials which would remove Am from solution but which were not included in the models.

Some qualitative successes were reported in predicting citrate and EDTA complexation effects, but there needs to be more work done in the area of organic complexation modeling as noted by Professor Kim, above.

The third stage of CHEMVAL addresses transport models. Since this is an exercise of a relatively new development in modeling, the test cases were very simple. A calcium speciation comparison showed the three participating codes reporting results so far, all using the CHEMVAL database, to yield essentially identical results. A uranium transport problem yielded essentially the same result when modeled using an analytical solution code and two of the same three codes used in the calcium speciation exercise. These three codes were also used to predict a pH profile in a cement at 200 years, and the results were similar. The third stage report is to be available later this year.

CHEMVAL's fourth stage is only just beginning. Two problems have been selected and are being defined: an Np column experiment and a flow-through study using sand.

The CHEMVAL database is being defined in support of the above activities. Results of critical database reviews are being used to formulate this standard database, which is to be made available in formats specific to the major participating codes. The Paris-based OECD's Nuclear Energy Agency's Thermodynamic DataBase (TDB) effort is represented at the MIRAGE Project's plenary meetings.

Research Area: IN-SITU EXPERIMENTS

Summary Overview of the Research Area

The summary overview of progress in this Research Area is Attachment 5. A number of the activities described in this progress report have already been discussed in Table 2, above. This is because in-situ experiments are being modeled, and therefore they were described as applications being made of calculational tools.

The correspondence between the In-Situ Migration Experiments described in Attachment 5 and the activities described in Table 2 is illustrated in Table 3. Table 3 also gives a very brief description of the work being done. Most of this work is site-specific, and may only be interesting to the Yucca Mountain Project from a methodology perspective.

Three in-situ experiment probes are being developed under CEC sponsorship, but only two of those under the auspices of the MIRAGE Project. The third probe, the Chromato probe, is mentioned at the end of Attachment 5. This third probe is a site-characterization tool to sample in-situ groundwater and concentrate naturally occurring Lanthanides into chromatographic columns. These columns are subsequently analyzed in the laboratory. Since Lanthanide behavior is comparable with Actinide behavior, information gained may be useful in predicting Actinide behavior in-situ.

Table 3. Correspondence between In-Situ Migration Experiments Described in Attachment 5 and Activities Listed in Table 2 (Attachment 4)

Attachment 5 Activity #	Title of Activity	Activity Description	Table 2 (Attachment 4) Activity #
2.1	<u>In-Situ Migration Experiments</u>		
	BRITISH GEOLOGIC SURVEY a) Aquifer characterization and instrumentation b) Laboratory studies c) Modeling	A study of migration in the relatively homogeneous sandy aquifer at the Driggs low-level waste site. The clay lenses of the study site have been described and the study of the natural organics and colloids in this system. Laboratory and modeling studies complement the field work.	a) 2.1.1 b) 2.2.2 c) 2.2.2
	SCK-CEN-Mol (Belgium) a) Labelled clay cores emplaced in boreholes b) Tracer injection with piezometer nest	Soluble radionuclides between two clay plugs are emplaced in boreholes to migrate with site groundwater. In-situ parameters are measured for Eu, Sr, Cs, Co, & U. Tracer (tritiated water first, I next) is injected under pressure and monitored.	a) 2.1.5 b) 2.1.5
	UKAEA-Harwell Chemistry Div.	Planned laboratory work on reconstituted clays to be complemented with field tests.	Not in Table 2
2.2	<u>Laboratory simulation experiments (JRC-ISPRA)</u>	Laboratory experiments using site-specific materials from Mol, Belgium and Gorleben, F.R.G.	Not in Table 2
2.3	<u>Geochemical probes</u> <u>CEA; CEN-Cadarache, France)</u> a) Foralab in-situ column probe b) Autolab diffusion-column probe	The Foralab probe is a forced-flow column filled with material of interest, placed in a borehole at depth and equilibrated with groundwater. Then it is sealed, radionuclide is injected, and the column top is sampled. The Autolab probe is a non-convecting column system for in-situ diffusion experiments.	Not in Table 2

Research Area: NATURAL ANALOGUES

Summary Overview of the Research Area

The summary overview of progress in this Research Area is Attachment 6. A quick overview of the topics discussed in Attachment 6 is provided in Table 4.

Preliminary findings from these studies have included useful insights into the perils of using geochemical models with databases that do not include the solid phases actually observed in the natural system. Results can be misleading and inappropriately suggest the presence or absence of solubility-controlling phases.

There is a trend toward the use of the U-series radionuclides as analogs for waste radionuclides in all of the activities described in Table 4. The experience being gained in the use of data concerning these elements may be of interest to the Yucca Mountain Project. The use of natural analogs in performance assessments was described as ranging from the "mildly confidence-building" to the "'final test' of our ability to build realistically predictive models."

MEETING EVALUATION

It seems to the traveler that the MIRAGE Project is doing work that is potentially useful to both the DOE's Civilian Radioactive Waste Management and Defense Programs. The MIRAGE efforts in defining and quantifying radionuclide interactions with naturally occurring and reprocessing organics seem particularly likely to be of interest to those working in the low level and transuranic waste disposal geochemistry and performance assessment areas. The work relating to salt dome overburden experimental geochemistry and modeling may or may not be of interest to those assessing the performance of the Waste Isolation Pilot Plant, depending on how the geochemistries of the MIRAGE study site (Gorleben, F.R.G.) and the New Mexico site compare.

Not many activities included in the MIRAGE work will produce results specifically or directly applicable to the OCRWM's Yucca Mountain Project. This is so because geochemical processes define radionuclide transport in ways that are specific to the physical and geochemical characteristics of a given setting. Nevertheless, the work being done in the verification and validation of geochemical codes should be useful in documenting and supporting the geochemical calculations done for the Yucca Mountain site. The work done to evaluate and experimentally determine thermodynamic data could be useful to geochemical modelers. Much of the work done in the field and natural analog studies reporting under MIRAGE may be of only peripheral interest to Yucca Mountain experimentalists and modelers. Interest would probably be focused on the experience being gained in the use of characterization methods, rather than on the outcome of the experiments being conducted. Finally, the work done in calculational and experimental methods development may have some limited applicability for Yucca Mountain, particularly in the modeling and characterization of the far field saturated zone.

Table 4. Status of Natural Analogue Work Performed Under the CEC's MIRAGE Project
(Numbers keyed to Attachment 6)

Activity #	Descriptive	Purpose, Status and Planned Work
2.1.1	Large-scale fluid movement in the Plio-Pleistocene blue clays of Italy	This work involves characterizing the subject clays in terms of fractures, mineral deposits, redox of percolating waters, hydrothermal systems, and regional tectonics. Relationships between deep-source gases and faulting is part of current work. A guide to data is being published. Future work may determine the preservation mechanisms that have allowed million-year old tree stumps to remain in nearly their original state. Organics and the behavior of natural radionuclides may also be investigated.
2.1.2	Smaller-scale elemental migration in sediments	U-series work on the cm to m scale in Scottish sediments with adjacent U mineralization, and in deep sea sediments with U-rich redox fronts. A diverse dataset of U-series migration under a variety of conditions is being generated. Work is at various states of progress at the three surface-sediment sites and the one deep-sea sediment site.
2.2.1	Elevated temperature migration in granitic rocks	A study of global mobilization and retention of U-series and other elements in and around a fossil hydrothermal vein in granite. The potential importance of phosphate minerals and complexes as actinide sorbers and transporters, respectively, is indicated by the data from one location. A second location has yielded information suggesting that U-series elements were mobilized during the thermal phase but immobilized again as the rock mass cooled, generally only millimeters from the zone of mobilization. The role of carbonates, oxides and clays in fixing U, Th, and other elements seemed indicated by the data.
2.2.2	Matrix diffusion in granitic rocks	It may be assumed that the entire volume of granitic rock is available for "matrix diffusion" in radionuclide transport modeling, resulting in significant migration impacts. Experiment does not often bear out this assumption, however, and this program seeks to characterize the micro-fracture properties of granitic rocks.

RECOMMENDATIONS

It is recommended that OCRWM continue to monitor and observe progress in the MIRAGE Project because, as noted, some MIRAGE work may be useful and of benefit to the Yucca Mountain Project. Work that is potentially useful and beneficial to the Yucca Mountain Project has been highlighted in the body of this Foreign Trip Report.

The traveler was recommended to attend this MIRAGE meeting because he serves as the lead person for the Total System Performance Working Group, an entity that serves to integrate and coordinate system performance activities that is located organizationally within the OCRWM Office of Systems Integration and Regulation's Regulatory Compliance Branch. Since the MIRAGE meeting, however, radionuclide transport work has been transferred from the Total System Performance Working Group into a newly formed Site Characteristics Assessment Working Group. This newly formed group is to bridge the site characterization and the performance assessment functions, and would thus be concerned with both field, laboratory, and modeling work that may affect performance assessments. It is recommended that the next MIRAGE meeting be attended by Ken Krupka, a geochemist, who is the leader of the new Site Characteristics Assessment Working Group.

APPENDIX

ITINERARY

<u>Dates</u>	<u>Location</u>	<u>Contacts</u>	<u>Topics</u>
3/14/89- 3/15/89	Travel from Washington, DC, to Brussels, Belgium		
3/16/89- 3/17/89	Brussels, Belgium	MIRAGE Meeting Attendees	MIRAGE Agenda Items
3/18/89- 3/20/89	Brussels, Belgium	None (3-day extra stay saved \$ 900 in air fare)	Weekend and vacation days
3/21/89	Return to Washington, DC		

PERSONS CONTACTED

CEC member nation attendees at the MIRAGE Project meeting, and invited observers from non-CEC nations such as Canada and Sweden.

APPENDIX (Cont.)

LITERATURE ACQUIRED

Commission of the European Communities Report RWD 89/1: Geological Disposal of Radioactive Waste, Annual Progress Report 1988.

This report is a to become a part of the Report EUR 12141 EN, available from the CEC later this year. The subjects covered by this particular contribution to EUR 12141 EN are:

Part A. Task 4: Research in support of the development of disposal facilities. 1988 progress in the CEC's radioactive waste research areas addressing site selection and characterization; repository and engineered barrier design and development; radionuclide migration; and shallow land burial.

Part B: Underground pilot facilities for the disposal of high-level radioactive waste. Progress at the Asse salt mine near Braunschweig, FRG, and the clay site near Mol, Belgium, are described for 1988.

Since this is a volume of 372 pages, interested parties may borrow this report from me on a first come - first served basis, but photocopies will not be made available.

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CEC Project MIRAGE - Second Phase

Second Plenary Meeting, Brussels, 16-17th March 1989

PROGRAMME16th MARCH

9.00 - 9.30 Introduction (CEC)

SESSION 1. Chairman: M. GINNIFF, UK-NIREX Ltd

9.30 Research Area "Geochemistry of Actinides and Fission Products"

9.30 - 10.30 Summary review (J.I. KIM)

10.30 - 11.00 Break

11.00 - 11.30 GRIMSEL Colloid Benchmark (C. DEGUELDRE)

11.30 - 12.30 Discussion

12.30 - 14.00 Lunch

SESSION 2. Chairman: B. SKYTTE-JENSEN, RISØ NL

14.00 Research Area "Calculation Tools"

14.00 - 14.50 Summary review (G. de MARSILY)

14.50 - 15.40 CHEMVAL (T. BROYD, D.READ - WS ATKINS E.S.)

15.40 - 16.00 Alternative approaches for treating uncertainty in
migration models (W. SHAW, Exploration Consultants Ltd)

16.00 - 16.30 Break

16.30 - 17.30 Discussion

17.30 Adjourn.

17th MARCH

SESSION 3. Chairman: C. DEL OLMO, ENRESA

8.45 Research Area "In-situ Experiments"

8.45 - 9.30 Summary review (A. AVOGADRO)

9.30 - 10.30 Discussion

10.30 - 11.00 Break

11.00 Research Area "Natural Analogues"

11.00 - 11.45 Summary review (N. CHAPMAN)

11.45 - 12.45 Discussion

12.45 - 13.00 Closure (CEC)

13.00 End of the meeting

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DRAFT
March 1989

COMMUNITY PROJECT MIRAGE (Second Phase)

*Plenary Meeting
Brussels, March 16 and 17, 1989*

Review of Work done in

RESEARCH AREA No.1

**GEOCHEMISTRY OF ACTINIDES AND FISSION PRODUCTS
IN NATURAL AQUIFER SYSTEMS**

BY J. I. KIM

This paper is a preliminary draft to be used only as a working document in the plenary meeting

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1. INTRODUCTION

The research area deals with the basic chemical behaviour of actinides and fission products in natural aquifer systems, which is indispensable to an understanding of primary mechanisms of the radionuclide migration in the geosphere. During the second phase of COMMUNITY PROJECT MIRAGE in research area No. 1 has been coordinated by the CEC to treat three important subjects which can be solved better by joint efforts and, at the same time, are of common interest to all participating laboratories. The coordinated research subjects are:

- (1) Complexation with natural and man-made organics
- (2) Colloid generation in groundwater
- (3) Basic retention mechanisms in aquifer systems

Initially research area No. 1 included the first two subjects. The abbreviation of "Complexation and Colloid" resulted in an unexpectedly charming description "COCO-Club" for the working group involved in research area No. 1. The first club members were BGS, CEA-FAR, JRC-Ispra, KUL, RISØ and TUM. This has now grown to include 14 different laboratories from the CEC member countries participating directly to research area No. 1 and 7 associate laboratories joining indirectly. In addition 4 laboratories from non-CEC member countries are also cooperating in the first two subjects. A list of all participating laboratories and their research interests in this research area is illustrated in Tables 1 and 2. In total, 20 research proposals, either under contract with the CEC or without contract, belong to research area No. 1 at this time. They are coordinated by the CEC to promote interlaboratory interactions as well as to facilitate the attainment of important results of common interest to all participating laboratories. For this purpose the three particular subjects above mentioned are coordinated and organized as summarized in Table 3.

The participation of individual laboratories in each of the research subjects mentioned here can be found in a summary table given in Appendix 1. The present review summarizes progress made until the end of 1988 in each research subject in a consolidated form, rather than the activities of each individual laboratory separately.

Table 1. Participating Laboratories in Research Area No. 1 of the Project MIRAGE II on the Geochemistry of Actinides and Fission Products in Aquifer Systems.

- (1) = Complexation with organics
- (2) = Colloid generation in groundwater
- (3) = Basic retention mechanisms in aquifer systems

Laboratories	(1)	(2)	(3)	Contract No.
1 BGS-I (Williams)	x	x		F11W/0064
2 BGS-II (Williams)	x		x	F11W/0203
3 CEA (Billon)	x	x		F11W/0068
4 CEN-SCK (Henrion)	x		x	F11W/0055
5 ENRESA (Astudillo)	x	x	x	F11W/0230
6 GSF-IFH (Fritz)			x	F11W/0210
7 Imperial College (Rees)	x		x	F11W/0147
8 JRC-Ispra (Avogadro)	x	x	x	CEC lab.
9 KUL (Cremers)	x			---
10 Univ. Nantes (Pierré)	x			F11W/0197
11 RISØ (Carlsen)	x		x	F11W/0066
12 TUM-I (Kfm)	x	x		F11W/0067
13 TUM-II (Kfm)			x	F11W/0202
14 UKAEA-I (Ewart)	x		x	F11W/0156
15 UKAEA-II (Ivanovich)		x		F11W/0234
16 UKAEA-CEA (Ramsay-Billon)		x	x	F11W/0204
17 AECL (Sargent)	x	x		*
18 PSI (Degueldre)		x		*
19 Univ. Linköping (Allard)	x			*
20 VTT (Vuorinen)		x		*
Associated Laboratories				association to
21 F.U. Berlin (Marx)				13**
22 CIEMAT (Rivas Romero)				5
23 KFK (Kanelakopoulos)				13
24 Univ. Mainz (Trautmann)				13
25 NAGRA (McKinley)				18
26 SKB (Ahlström)				19
27 Univ. Loughborough (Warwick)				2

* Work performed in the framework of a cooperative agreement with the CEC

** The number refers to the leading laboratories

Table 2. Laboratory abbreviation: participating laboratories in research area No. 1 of the project MIRAGE II

AECL:	Atomic Energy of Canada Ltd., Manitoba (Canada)
BGS:	British Geological Survey, Keyworth (UK)
CEA-FAR:	Commissariat a l'Energie Atomique, Fontenay aux Roses (F)
CEN/SCK:	Centre d'Etude de l'Energie Nucleaire/Studiecentrum voor Kernenergie, Mol (B)
CIEMAT:	Centro de Investigaciones Energéticas Medioambientales y Tecnológicas, Madrid (E)
ENRESA:	Empresa Nacional de Residuos Radioactivos, Madrid (E)
FUB:	Freie Universität Berlin, Berlin (FRG)
GSF-IFH:	Gesellschaft für Strahlen- und Umweltforschung, Institut für Hydrologie, München (FRG)
ICL:	Imperial College, London (UK)
JRC-Ispra:	Joint Research Centre, Ispra (CEC)
KFK-IFCh	Kernforschungszentrum Karlsruhe, Institut für Heiße Chemie, Karlsruhe (FRG)
KUL:	Katholieke Universiteit Leuven, Leuven (B)
NAGRA:	Nationale Genossenschaft für die Lagerung radioaktiver Abfälle, Baden (CH)
PSI:	Paul Scherrer Institut, Würenlingen (CH)
RISØ:	Risø National Laboratory, Roskilde (DK)
SKB:	Swedish Nuclear Fuel and Waste Management, Stockholm (S)
TUM:	Technische Universität München, Garching (FRG)
UKAEA:	United Kingdom Atomic Energy Authority, Harwell (UK)
U Linköping:	University of Linköping, Linköping (S)
U Loughborough:	University of Loughborough, Loughborough (UK)
U Mainz:	Universität Mainz, Mainz (FRG)
U Nantes:	Universitaire Nantes, Nantes (F)
VTT:	Technical Research Centre of Finland, Espoo (FIN)

Table 3. Coordinated Research Subjects in Research Area No. 1 of the Project MIRAGE II on the Geochemistry of Actinides and Fission Products in Aquifer Systems

1 Complexation with organics

1.1 Interlaboratory comparison exercise

- Characterization of reference commercial humic acids (HA)
- Characterization of site specific humic acids
- Complexation with reference commercial humic acids
- Complexation with site specific humic acids

1.2 Characterization of other natural organics

- Separation and characterization
- Complexation behaviour

1.3 Complexation with man-made organics, e.g. EDTA

2 Colloid generation in groundwater

2.1 Interlaboratory comparison exercise

- sampling
- characterization

2.2 Generation mechanisms

- Humic colloid generation
- Inorganic colloid generation
- Generation of real-colloids and pseudocolloids

3 Basic retention mechanisms in aquifer systems

3.1 Influence of natural organics and colloid generation on

- Solubility of radionuclides
- Sorption process
- Diffusion process

3.2 General sorption experiments

- Influence of redox conditions
- Comparison of different experimental processes (static, dynamic and diffusion processes)

3.3 Speciation

- Direct speciation by spectroscopy
- Indirect speciation by chemical separation

3.4 Compilation and evaluation of thermodynamic data

- Critical review on the role of organics
- Compilation, verification and determination of hydrolysis reactions and carbonate complexation

3.5 Theoretical prediction of sorption phenomena (Speciation modeling)

2. WORK REVIEW

The following review of the work carried out in the member laboratories is brought up to date and presented in the same order as the research subjects given in the introductory section (cf. Table 3).

2.1 Complexation with organics

The importance of the complexation of radionuclides with either natural organics or man-made organics to the migration of heavy metal ions of higher oxidation states ($Z \geq 2+$) in natural aquifer systems is widely recognized [Kim 1986; Choppin 1988; Carlsen 1988]. Among a wide variety of natural organics the preponderous species in groundwater are humic and fulvic acids, both of which are polyelectrolytes with a high complexation affinity [Kim 1986; Moulin 1986; Carlsen 1988; Cremers et al. 1988; Choppin 1988]. These two acids are structurally similar but different in molecular weight and functional group content [Kononova 1961; Stevenson 1972; Schnitzer and Kahn 1972]. In groundwater, soluble humic substances, including humic and fulvic acids, are already complexed with metal ions of water constituents, e.g. Fe^{3+}/Fe^{2+} , Ca^{2+} , REE-ions etc. and are present as humic colloids [Kim et al. 1987]. These colloids act, then, as soluble exchangers and hence create pseudocolloids of actinide ions [Kim et al. 1987; Ramsay 1988]. Such humic colloids or pseudocolloids is separable easily from the solution by ultrafiltration. Humic substances may thus cause an enhancement of migration, or retention, of some radionuclides in a given aquifer system. For the quantification of each of these processes, a basic knowledge of the nature of humic and fulvic acids and their complexation behaviour under groundwater conditions is indispensable. For these obvious reasons, a joint action in the field of characterization of humic acids and complexation of radionuclides has been launched in the project MIRAGE II. The results obtained until the end of 1988 are discussed below.

2.1.1 Interlaboratory comparison exercise for the characterization of humic acids

At the beginning in 1986 five laboratories (BGS, CEA-FAR, JRC-Ispra, RISØ and TUM) joined this exercise to characterize three different humic

acids which were prepared and distributed by TUM. The detailed report of each laboratory is to be found elsewhere [Moulin et al. 1988; Bidoglio 1987; Peachy and Williams 1988; Carlsen 1988; Kim and Buckau 1988]. Later AECL joined the part of the exercise. The purpose of this exercise is to compare the different analytical procedures of the participating laboratories with one another and thus to produce well substantiated physical and chemical data for particular humic acids. The humic acids taken for the first stage of the exercise are:

- (a) reference commercial humic acids from ALDRICH Co.
 - original form: HA(Na⁺)-Aldrich
 - purified and protonated: HA(H⁺)-Aldrich

- (b) site-specific humic acid extracted from a Gorleben groundwater
 - purified and protonated: HA(H⁺)-Gohy 573

Table 4 summarizes the physical and chemical properties characterized by different laboratories for the humic acids given above. In the meantime the number of laboratories participating in this exercise has grown to eight with the addition of AECL Canada, UKAEA Chem.I, UK and U. Nantes, France.

For the second stage of this exercise, another site-specific humic acid has been extracted by CEA-FAR from the groundwater of Fanay-Augeres and is being distributed only to 6 laboratories (TUM, JRC-Ispra, RISØ, BGS, UKAEA-Chem.I, U. Link.). Because of the limited supply of the material [Moulin 1988], the characterization is being made by CEA-FAR and TUM and other laboratories will join the complexation study only.

The site-specific humic acid from the Boom clay at the Mol area was once extracted and distributed by KUL. Because of its extremely large molecular size, this humic acid was difficult to purify properly and, once purified and solidified, was not easily soluble in water under normal conditions. For this reason a new attempt was made by GEN-SCK to extract "aqueous" humic acid from the Boom clay. This humic acid concentrate (40 L volume) was sent to TUM for purification and solidification. The final product obtained is ca. 1.5 g, which is too small to be characterized by many laboratories. The characterization is being made by TUM only and

Table 4. Interlaboratory comparison exercise for the characterization of humic acids: characterization subjects and participating laboratories

Subject	BGS	CEA- FAR	ENR- ESA	JRC Ispra	Nantes Univ.	RISØ	TUM	UKAEA Chem. I	AECL
1. Chemical composition									
- H ₂ O content	x	x	o	x		x	x		x
- Element composition: CHNOS	x	x	o	x			x		x
- Metal content (major/trace)	x	x	o	x		x	x		x
2. Proton capacity (meq/g)									
- Total capacity	x	x	o	x		x	x		
- Carboxyl group	x	x	o	x		x	x		
- Phenol group	x	x	o	x		x	x		
3. Spectroscopic characteristics									
- UV-spectrum: humification state	x	x	o	x			x		
- IR-spectrum: functional group		x	o	x			x		
- NMR-spectrum: functional group							x		
4. Size distribution									
- Gel chromatography		x			x		x	x	
- Ultrafiltration	x	x	o	x			x		
- Ultracentrifugation				x	x		x	x	

x) active participation; o) expected to participate

the rest substance is available for the complexation study which requires relatively a small amount.

The two new humic acids included are:

(c) site-specific humic acid extracted from a Fanay-Augères groundwater
- purified and protonated: HA(H⁺)-Fanay-Augères

(d) site-specific humic acid extracted from Boom-Clay pore water
- purified and protonated: HA(H⁺)-Boom Clay

Apart from above mentioned reference and site-specific humic acids, fulvic acids are also extracted from the same groundwaters for the future study. They are:

(e) site-specific fulvic acid extracted from a Gorleben groundwater
- purified and protonated: FA(H⁺)-Gohy 573

(f) site-specific fulvic acid extracted from a Fanay-Augères groundwater
- purified and protonated: FA(H⁺)-Fanay-Augères

(g) site-specific fulvic acid extracted from Boom-Clay pore water
- purified and protonated: FA(H⁺)-Boom Clay

The fulvic acids (e) and (g) are available from TUM (Buckau) and (f) from CEA-FAR (Moulin).

The first stage exercise with the above mentioned three humic acids, (a) and (b) from TUM, has produced data which are found to be quite satisfactory. Due to the lack of space in this review paper, some important features of the results are presented without commenting in great detail on the analytical procedures and problems involved in the individual characterization. An inclusive report on the interlaboratory comparison exercise for the characterization of humic acids are published separately [Moulin et al. 1988; Bidoglio 1987; Peach and Williams 1988; Carlsen 1988; Kim and Buckau 1988; Pieri 1988; Ewart et al., 1989].

Some results being available for the moment from the characterization of HA(H⁺)-Fanay-Augères and HA(H⁺)-Boom Clay are also included for the comparison of characteristics of different humic acids.

(I) Humidity content

Humic acids contain certain amounts of moisture, when they are left in contact with air moisture; the content varies with the humidity of the surrounding atmosphere. The substances stored in airtight bottles after their preparation have been analysed by TUM with three different methods: desiccator-drying under vacuum, oven-drying at 75 °C and Karl-Fischer titration. The average values from these three experiments are given in Table 5 together with the values from other laboratories. The fluctuation of data from laboratory to laboratory is significant, which is ascribed to different handling and moisture contents in each laboratory. All analytical results must be, therefore, corrected in accordance with the moisture contents determined for the substances in each experimental condition.

Table 5. Comparison of moisture contents in different humic acids used for the inter-laboratory comparison exercise (%)

Humic Acid	TUM	JRC-Ispra	CEA-FAR	BCS	RISØ	AECL
HA(Na ⁺)-Aldrich	16.3 ± 1.1	12.4	25	18.9	12.1	23 ± 4
HA(H ⁺)-Aldrich	6.6 ± 0.3	10.7	4	8.5	4.8	-
HA(H ⁺)-Gohy 573	7.2 ± 0.1	-	4	7.5	4.3	-
HA(H ⁺)-Fanay-Augères	-	-	9	-	-	-

(II) Chemical composition

The major element composition analysed for HA(Na⁺)-Aldrich, HA(H⁺)-Aldrich and HA(H⁺)-Gohy 573 are, as shown in Table 6, in reasonably good agreement with one another. Average values with relative standard deviations given on the right side of each table reflect the precision of in-

Table 6. Comparison of major element contents of humic acids used for the interlaboratory comparison exercise (%)

HA(Na ⁺)-Aldrich						
Element	TUM	JRC-Ispra	CEA-FAR	BCS	AECL	Average
C	41.72	40.05	39.73	39.43	(46.34)	40.23 ± 1.02
H	4.37	3.75	4.67	3.37	(4.48)	4.04 ± 0.59
N	0.25	0.50	0.44	0.44	(1.97)	0.41 ± 0.11
O	36.93	32.69	38.52	-	(30.4)	36.05 ± 3.01
S	1.90	1.88	1.95	-	(2.27)	1.91 ± 0.04
Rest	14.83	21.49	22.60	-	(14.54)	19.64 ± 4.20

HA(H ⁺)-Aldrich					
Element	TUM	JRC-Ispra	CEA-FAR	BCS	Average
C	53.44	54.02	56.00	53.06	54.13 ± 1.31
H	4.34	4.65	4.28	3.87	4.29 ± 0.32
N	0.31	1.05	0.72	1.66	0.94 ± 0.57
O	36.43	33.85	34.60	-	34.96 ± 1.33
S	2.25	2.30	2.23	-	2.26 ± 0.04
Rest	3.23	4.13	2.17	-	3.18 ± 0.98

HA(H ⁺)-Cohy 573					
Element	TUM	JRC-Ispra	CEA-FAR	BCS	Average
C	56.11	55.28	55.23	54.25	55.22 ± 0.76
H	4.46	4.38	4.77	4.03	4.54 ± 0.21
N	1.68	1.72	1.80	1.66	1.72 ± 0.06
O	35.16	35.22	33.73	-	34.70 ± 0.84
S	1.76	1.71	1.65	-	1.71 ± 0.06
Rest	0.83	1.79	2.82	-	1.81 ± 1.00

(): Values not included in the average values

Table 7. Comparison of average elemental contents of humic acids: dried and ash-free basis(%)

Element	HA(Na ⁺)-Aldrich	HA(H ⁺)-Aldrich	HA(H ⁺)-Cohy 573	HA(H ⁺)-Fanay-Augères	HA(H ⁺)-Boom Clay ***	Lit. Value [Stevenson 1982]
C	48.7 ± 1.0 (56.2)*	56.0 ± 1.3	56.4 ± 0.8	47.4 (46.2)**	62.4 ± 0.1	50 - 60
H	4.9 ± 0.6 (4.4)	4.4 ± 0.3	4.6 ± 0.2	7.1 (6.9)	6.1 ± 0.1	4 - 6
N	0.5 ± 0.1 (0.6)	1.0 ± 0.6	1.8 ± 0.1	8.2 (8)	2.9 ± 0.1	2 - 6
O	43.6 ± 3.0 (36.2)	36.2 ± 1.3	35.4 ± 0.8	34.5 (33.6)	27.0 ± 0.2	30 - 35
S	2.3 ± 0.1 (2.6)	2.3 ± 0.1	1.7 ± 0.1	2.9 (2.8)	1.7 ± 0.2	0 - 2

()*: Values normalized on the assumption that the oxygen and hydrogen contents are the same as the value found in HA(H⁺)-Aldrich; (**): Original values [Moulin 1988]; (**): Values from TUM [Kim, Buckau 1989]

dividual values. The uncertainty in the oxygen content of HA(Na⁺)-Aldrich is the largest. This may be due to variations in the moisture determination and also to the large amounts of metal hydroxides or oxides present in this unpurified humic acid. Elemental contents of the humic acids including HA(H⁺)-Fanay-Augères and HA(H⁺)-Boom Clay are compared with the literature values [Stevenson 1982] in Table 7 after recalculating CHNOS values to be 100 %.

Values of the purified humic acids, HA(H⁺)-Aldrich and HA(H⁺)-Gohy 573 not only agree with each other but also are in good accord with the literature values. The elemental contents of HA(Na⁺)-Aldrich are distorted by the presence of a large amount of metal ion impurities (see Table 9). When these values are normalized to the oxygen and hydrogen contents of HA(H⁺)-Aldrich which is the purified humic acid of HA (Na⁺)-Aldrich, the resulting values, particularly the carbon content, are in better agreement with the values of other humic acids. The somewhat higher oxygen (43.6 %) and hydrogen values (4.9 %) in HA(Na⁺)-Aldrich suggest that much of metal impurities are in a hydroxide form. The excess contents of oxygen and hydrogen in HA(Na⁺)-Aldrich, being related to their values in HA(H⁺)-Aldrich, give rise to an atom ratio of O/H about 0.93, which supports the metal hydroxide as involved impurities. The results given in Table 7 provide assurance that the humic acids, HA(H⁺)-Aldrich and HA(H⁺)-Gohy 573 are, as far as element composition is concerned, nearly the same as other humic acids [Stevenson 1982; Steelink 1985].

Element compositions of HA(H⁺)-Fanay-Augères and HA(H⁺)-Boom Clay are distinctively different from the values of HA(H⁺)-Aldrich and HA(H⁺)-Gohy 573. Atom ratios of H/C, O/C and N/C for the humic acids are summarized in Table 8.

The atom ratio of H/C is indicative of the chemical state of humic acid. For pure aromatics (C_nH_n) the ratio is 1.0, whereas the ratio becomes greater than 2.0 for pure aliphatics. In mixed complexes, as is the case for humic acid in general, aliphatic as well as primary amino components increase the H/C atom ratio, while carboxyl, ester and ether components decrease the ratio. H/C ratios are clustered around 1.0 for most soil and aquatic humic and fulvic acids. Sedimentary humic acids have some-

what higher H/C ratios (up to 1.4) than their soil or water counterparts and ratios above 1.3 indicate that the material may contain a nonhumic substance [Steelink 1985].

The O/C ratio is the clearest indicator of humic groups. Soil humic acid ratios cluster around 0.5 while soil fulvic acids center around 0.7. Aquatic humic acids are close to the soil humic acid ratio of 0.5, whereas aquatic fulvic acids possess lower ratios around 0.6. When groundwater humic acids show abnormally low O/C ratios, this may be due to contamination by Kerogens or Trona acids. [Steelink 1985].

The N/C ratio is varying much from humic acid to humic acid but an average value is found to be 0.04 for both soil and aquatic humic acids. For fulvic acids an average value is slightly less (0.03) [Steelink 1985].

Table 8. Atomic ratios of elements in humic acids

Humic acid	H/C	O/C	N/C
HA(H ⁺)-Aldrich	0.94 ± 0.07	0.48 ± 0.02	0.02
HA(H ⁺)-Gohy 573	0.98 ± 0.05	0.47 ± 0.01	0.03
HA(H ⁺)-Fanay-Augères	1.80	0.55	0.15
HA(H ⁺)-Boom Clay	1.17 ± 0.02	0.32 ± 0.01	0.04
HA(H ⁺)-General [Steelink 1985]	1.0	0.5	0.04
FA(H ⁺)-General [Steelink 1985]	1.0	0.6 ~ 0.7	0.03

According to the literature data [Steelink 1985], HA(H⁺)-Aldrich and HA(H⁺)-Gohy 573 belong to the normal category of humic acids, whereas HA(H⁺)-Fanay-Augères resembles sedimentary humic substances. HA(H⁺)-Boom Clay appears similar to the humic acid from Fox Hill groundwater [Thurman and Malcom 1981].

(III) Metal ion impurities

The metal ion concentrations contained in HA(Na⁺)-Aldrich, HA(H⁺)-Aldrich and HA(H⁺)-Gohy 573 are given in Table 9. Analyses from five different laboratories agree reasonably well with one another for major

Table 9. Comparison of metal concentrations in humic acids used for the interlaboratory comparison exercise (ppm)

HA(Na ⁺)-Aldrich						
Element	TUM	JRC-Ispra	CEA-FAR	BCS	RISØ	AECL
Al	2950 ± 60	3443 ± 141	3100	3400/3700	-	3800
Ba	91 ± 4	158 ± 4	200	-	140	-
Ca	9931 ± 89 8610 ± 808	10104 ± 182	6600	8500	6000	10400
Cr	15.2 ± 0.1	25 ± 3.2	100	-	14.7	-
Fe	12207 ± 651	12152 ± 49	14600	12700/11350	13000	14400
Mg	698 ± 25	811 ± 11	(1500)	690/750	883/893	900
Mn	24 ± 2	36 ± 11	100	35/36	33/34	-
Na	75116 ± 140 86248 ± 2184	88547 ± 1417	90000	82650/85000	72000	111000
Si	3333 ± 185	2500	6300	-	5000	4800

HA(H ⁺)-Aldrich					
Element	TUM	JRC-Ispra	CEA-FAR	BCS	RISØ
Al	35	23 ± 11	<10	13/31	-
Ba	-	2.0 ± 0.6	<10	-	0.78
Ca	31.7 ± 6.7	127 ± 27	60	41/48	125
Cr	12.1 ± 0.1	12.3 ± 0.6	50	-	2.1
Fe	360 ± 13 357 ± 5	578 ± 106 365 ± 35	390	310/482	420
Mg	5.6 ± 2.0	16 ± 7	<1	4/5	0.6
Mn	-	25 ± 21	-	5/8.7	-
Na	270 ± 2	271 ± 10	350	223/333	-
Si	15 ± 8	41	840	-	-

HA(H ⁺)-Gohy 573					
Element	TUM	JRC-Ispra	CEA-FAR	BCS	RISØ
Al	7.3	64.6	<10	19/21	-
Ca	22.6 ± 5.6	66.7	26	41	42
Cr	101 ± 1	118.5	200	-	4.9
Fe	282 ± 13	342	330	278/321	370
Mg	4.2 ± 0.9	8.5	<1	4	-
Mn	-	1.9	1	1	<0.01
Na	19.0 ± 0.1	20.6	<10	14	-
Si	68 ± 19	-	820	-	-

elements, e.g. Al, Ca, Fe and Na. For minor elements, discrepancies in analytical results are relatively large. In order to compare concentrations of inorganic elements in the three humic acids, the weighted mean values of each element are evaluated taking account of a weighting factor for each laboratory value. A weighting factor of five is given to the TUM values and three to the JRC values, because they are determined in quintuplicate and in triplicate, respectively. All other values are assigned a weighting factor of one for each; this applies also to the JRC values of HA(H⁺)-Gohy 573.

The weighted mean values from Table 9 are given in Table 10 together with the values known for HA(H⁺)-Fanay-Augères [Moulin 1988] and HA(H⁺)-Boom Clay [Kim and Buckau 1989]. From the data shown in this table, metal ions loaded on the unpurified humic acid, HA(Na⁺)-Aldrich, are found to be 0.31 meq./g of Al³⁺, 0.47 meq./g of Ca²⁺, 0.67 meq./g of Fe³⁺ and 3.6 meq./g of Na⁺. The silicium content amounts to 3.5 mg/g. The total metal ion concentration gives rise to a value of 5.1 ± 0.4 meq./g, which is fortuitously very close to the value of the carboxylic proton capacity (see below). The purification results in a drastic decrease in the concentrations of these elements, mostly to less than 1 % except for Fe which remains still about 3 % of the initial amount. The minor elements, e.g. Cr, Mn, do not show a distinctive concentration change. In the two purified humic acids, HA(H⁺)-Aldrich and HA(H⁺)-Gohy 573, the metal ion impurities are present in a very small concentration, suggesting that all functional groups are quantitatively (>99 %) protonated in the purification process. It is to be noted that the last trace amount of Fe is difficult to remove from humic acid by acid treatment and remains in the range of 15 ~ 30 µeq/g. This is about 0.3 ~ 0.5 % of the total proton capacity of a given humic acid, and thus will not be a hindrance to the complexation study.

Concentrations of metal impurities in HA(H⁺)-Fanay-Augères and HA(H⁺)-Boom Clay are substantially higher than in HA(H⁺)-Aldrich and HA(H⁺)-Gohy 573, especially concentrations of Al, Fe, Cr, Zn, Si and U. The high concentration of U in HA(H⁺)-Fanay-Augères explains its origin from an uranium mine and also a strong complexation of U with humic acid. Con-

Table 10. Weighted mean concentrations of metal ions in humic acids used for the interlaboratory comparison exercise (ppm)

Element	HA(Na ⁺)-Aldrich	HA(H ⁺)-Aldrich	HA(H ⁺)-Cohy 573	HA(H ⁺)-Fanay-Augères	HA(H ⁺)-Boom Clay
Al	2817 ± 1022	28.8 ± 7.8	10.9 ± 6.2	340	1142 ± 41
Ba	126 ± 41	1.7 ± 0.6	-	-	-
Ca	9486 ± 760	67.8 ± 44.2	27.8 ± 8.6	5080	27.5 ± 3.6
Cr	18.4 ± 4.9	12.2 ± 0.1	117 ± 37	-	222.5 ± 0.7
Fe	12428 ± 784	410 ± 89	305 ± 33	670	2415 ± 30
Mg	762 ± 77	8.5 ± 5.2	4.8 ± 1.6	2200	88.6 ± 1.9
Mn	35.1 ± 1.2	17.7 ± 10.0	1.3 ± 0.5	10	-
Na	83456 ± 6399	279 ± 34	18.2 ± 2.0	900	76 ± 36
Si	3546 ± 1211	24.8 ± 13.5	68 ± 19	400	2590 ± 123
U	0.65 ± 0.01	0.23 ± 0.01	2.2 ± 0.1	7760	17.0 ± 0.9
Zn	12.0 ± 0.2	2.6 ± 0.2	2.7 ± 0.3	1200	34.8 ± 0.6

Table 11: Inorganic trace impurities in humic acids (ppm): determined by NAA

Element	HA(Na ⁺)-Aldrich	HA(H ⁺)-Aldrich	HA(H ⁺)-Cohy-573	HA(H ⁺)-Boom-Clay
Ag	-	0.04	0.17 ± 0.01	5.63 ± 0.04
As	1.14 ± 0.09	0.16 ± 0.01	2.33 ± 0.04	-
Br	8.7 ± 0.1	13.1 ± 0.1	63 ± 2	350 ± 2
Ce	23.0 ± 0.2	4.1 ± 0.3	1.1 ± 0.2	10.1 ± 0.5
Co	2.5 ± 0.1	0.33 ± 0.01	2.5 ± 0.1	8.5 ± 0.1
Cs	0.27 ± 0.01	-	-	0.26 ± 0.01
Eu	0.66 ± 0.02	0.24 ± 0.01	0.05 ± 0.001	0.22 ± 0.002
Hf	0.38 ± 0.01	0.06 ± 0.01	1.53 ± 0.01	9.50 ± 0.08
Hg	-	1.8 ± 0.1	18.0 ± 0.3	4.0 ± 0.2
La	8.8 ± 0.1	0.90 ± 0.01	0.39 ± 0.01	-
Lu	0.13 ± 0.01	0.030 ± 0.002	0.14 ± 0.01	0.69 ± 0.04
Mo	0.98 ± 0.01	0.74 ± 0.02	12.6 ± 0.2	-
Nd	11.5 ± 0.3	4.1 ± 0.1	0.69 ± 0.01	-
Sb	0.09 ± 0.01	0.051 ± 0.002	0.15 ± 0.01	2.01 ± 0.01
Sc	2.6 ± 0.1	0.030 ± 0.001	0.55 ± 0.01	0.82 ± 0.01
Se	2.1 ± 0.1	2.20 ± 0.04	1.7 ± 0.2	15.7 ± 0.1
Sm	2.3 ± 0.1	0.98 ± 0.03	0.13 ± 0.01	-
Ta	0.11 ± 0.01	0.010 ± 0.001	0.30 ± 0.01	0.27 ± 0.01
Tb	0.26 ± 0.01	0.060 ± 0.001	0.05 ± 0.002	2.33 ± 0.01
Th	2.0 ± 0.1	1.53 ± 0.01	7.4 ± 0.1	9.29 ± 0.08
U	0.65 ± 0.01	0.23 ± 0.01	2.2 ± 0.1	17.0 ± 0.9
W	-	0.12 ± 0.01	4.4 ± 0.1	-
Yb	0.49 ± 0.01	0.10 ± 0.01	0.50 ± 0.02	2.66 ± 0.15
Zn	12.0 ± 0.2	2.6 ± 0.2	2.7 ± 0.3	34.8 ± 0.6
Zr	21 ± 2	4.6 ± 0.1	119 ± 3	251.4 ± 3.4

siderably high concentrations of Al, Cr, Fe and Zn in HA(H⁺)-Boom Clay, even after acid treatment, demonstrate that the exchange kinetics of these metal ions in humic acid are very slow. The large Si content in HA(H⁺)-Boom Clay is always observed.

To complete the purity control of HA(Na⁺)-Aldrich, HA(H⁺)-Aldrich, HA(H⁺)-Gohy 573 and HA(H⁺)-Boom Clay, all trace impurities are further analysed, as shown in Table 11. It is interesting to compare the concentrations of those trace elements, which are natural analogues of actinides and some fission products, in the non-purified humic acid HA(Na⁺)-Aldrich with that in the purified humic acid HA(H⁺)-Aldrich. They are difficult to remove completely by the acid purification treatment. However, in the purified humic acids, HA(H⁺)-Aldrich and HA(H⁺)-Gohy 573, the total concentrations of trace elements are so small that they will not disturb the complexation study of a given radionuclide with these humic acids.

(IV) Proton capacity

Of various functional groups associated with humic acids [Stevenson 1982], two important proton exchange derivatives are taken into consideration for the present interlaboratory comparison exercise, namely carboxyl and phenol groups. Measurements are carried out for the proton capacity of total, carboxyl and phenol exchange groups. Methods used are the Ba(OH)₂ procedure as well as direct pH titration in NaClO₄ for the total proton capacity and the Ca acetate procedure for the carboxyl group capacity [Schnitzer and Kahn 1972]. The difference between the total and carboxyl group capacities is taken to be the phenol group capacity. The latter represents, in fact, the capacity of all weak acid groups, of which the phenol group is known to be predominant.

Measurements of proton capacities from five laboratories are compared in Tables 12-14. The scattering of data from different laboratories reflects some serious difficulties involved in the measurement. The treatment of Ba(OH)₂ requires a careful discrimination against CO₂ absorption in the course of experiment. As shown in Table 12 the protonation of HA(Na⁺)-Aldrich appears not negligible, although all functional sites

Table 12. Total Proton Capacity determined by the $\text{Ba}(\text{OH})_2$ method (meq/g HA)

Humic Acid	TUM	JRC-Ispra	CEA-FAR	BCS	RISØ
HA(Na^+)-Aldrich	0.96 ± 0.64	-	-	0.65	(3.08)
HA(H^+)-Aldrich	7.06 ± 0.67	8.51 ± 0.91	9.3 ± 0.3	7.74	8.04
HA(H^+)-Gohy 573	6.61 ± 0.27	5.71	4.8 ± 1.2	6.42	6.94

Table 13. Proton Capacity of the Carboxyl group determined by the $\text{Ca}(\text{Ac})_2$ method (meq/g HA)

Humic Acid	TUM	JRC-Ispra	CEA-FAR	BCS	RISØ
HA(Na^+)-Aldrich	0.05	-	-	0	0.15
HA(H^+)-Aldrich	4.80 ± 0.21	3.96 ± 0.62	4.75 ± 0.40	5.56	4.69
HA(H^+)-Gohy 573	4.75 ± 0.29	4.65	4.27 ± 0.12	4.87	4.29

Table 14. Proton Capacity of the Phenol group evaluated from the $\text{Ba}(\text{OH})_2$ and $\text{Ca}(\text{Ac})_2$ methods (meq/g HA)

Humic Acid	TUM	JRC-Ispra	CEA-FAR	BCS	RISØ
HA(Na^+)-Aldrich	0.91 ± 0.64	-	-	0.65	(2.93)
HA(H^+)-Aldrich	2.26 ± 0.72	4.55 ± 1.10	4.55 ± 0.50	2.18	3.35
HA(H^+)-Gohy 573	1.86 ± 0.40	1.06	0.55 ± 1.21	1.55	2.65

Table 15. Comparison of average proton capacities (meq/g HA)

Humic Acid	Total Proton Capacity	Carboxyl group	Phenol group
HA(H^+)-Aldrich	7.84 ± 0.61	4.75 ± 0.65	3.09 ± 0.89
HA(H^+)-Gohy 573	6.42 ± 0.52	4.64 ± 0.25	1.78 ± 0.58
Range of Lit. Values*	5.60 - 8.90	1.50 - 5.70	2.10 - 5.70

* M. Schnitzer, in Proc. Symp. on Soil Organic Matter Studies, Braunschweig, IAEA (1977) pp. 117 - 131 [cf. Stevenson 1982].

are expected to be consumed by metal ion complexation. Since the protonation of carboxyl group of HA(Na⁺)-Aldrich seems to be negligible, the substantial proton capacity shown in Table 12 may be attributable to the phenol group (see Table 14) which contains protons in the unpurified state of humic acid: HA(Na⁺)-Aldrich. The total proton capacity of HA(H⁺)-Aldrich is found to be distinctively larger than that of HA(H⁺)-Gohy 573, although individual results are considerably scattered.

The proton capacities of carboxyl group shown in Table 13 for HA(H⁺)-Aldrich and HA(H⁺)-Gohy 573 are on average similar to each other. The carboxyl capacity of HA(Na⁺)-Aldrich is found to be negligible, presumably due to complete salt formation. The phenol group capacities from different laboratories (Table 14) are scattered considerably, because these data are derived from differences between the values in Table 12 and 13. The difference in total proton capacities between HA(H⁺)-Aldrich and HA(H⁺)-Gohy 573 results from the difference in their phenol group capacities (Table 14).

Average values of the data given in Tables 12-14 are summarized in Table 15 for HA(H⁺)-Aldrich and HA(H⁺)-Gohy 573 together with the ranges of literature values [Stevenson 1982] of each group. The proton capacities of the humic acids under consideration are all within the range of values found in the literature, except the phenol group capacity of HA(H⁺)-Gohy 573. The data given in Table 15 are applicable for the complexation study that is in progress at this time as a COCO club activity.

The total proton capacity has been also determined by four different laboratories using a direct pH titration in NaClO₄ solution. The results are shown in Table 16. Discrepancies among data are extreme. The main reason may be different interpretation of the titration results made in each laboratory. A second reason might be the experimental handling that differs one laboratory to another. In direct pH titration, the proton capacity of carboxyl group is derived from the main derivative peak. When interpreted in this manner, the value from the direct pH titration should correspond to that from the Ca acetate method within experimental uncertainty. Unfortunately this is not the case in the present interlaboratory comparison exercise.

Table 16. Proton capacity determined by a direct pH titration in NaClO₄ solution (meq/g)

Humic acid	TUM	JRC-Ispra	CEA-FAR	KUL	RISØ
HA(Na ⁺)-Aldrich	-	0.64	1.9	-	-
HA(H ⁺)-Aldrich	5.43 ± 0.16	5.24	6.0 ± 0.5	2.7/3.9	7.70 ± 0.11
HA(H ⁺)-Gohy 573	5.38 ± 0.20	-	5.2/5.2	3.5/4.5	10.44 ± 1.52
HA(H ⁺)-Fanay-Augères	-	-	3.4 ± 0.2	-	-
Condition	I = 0.1 and 1.0	I = 0.1	I = 0.1	pH = 7/10 I = 0.1	unknown

The proton capacity is the primary important chemical parameter of humic acid, which gives an insight into the complexation as well as ion exchange behaviour of the acid in a given aquifer system. The characterization of individual functional groups is of great interest for a better understanding of complexation mechanisms of humic acid with different metal ions. This will be pursued by the COCO group members.

(V) Spectroscopic characteristics

The literature contains much spectroscopic information [MacCathy and Rice 1985] related to the characterization of humic acids. Commonly used are UV, IR and NMR spectroscopies, each of which contributes segmentary information to the structural state of a given humic acid [Stevenson 1982].

< E4/E6 ratio >

UV spectrum of humic acids shows an absorption continuum, without recognizable peaks, increasing with decreasing wavelength. The E4/E6 value used widely to characterize humic acids is the ratio of absorption intensities at 465 and 665 nm. However, its interpretation is not straightforward. The E4/E6 ratio is supposed to decrease with increasing humification [Thurman 1985] or increasing condensation of aromatic humic constituents [Konnova 1966]. Other suggestions are that the E4/E6 ratio governed mainly by the particle size (or molecular weight) is dependent

Table 17. Humification parameter (E4/E6)

Humic acid	TUM	JRC-Ispra	CEA-FAR	BGS
HA(Na ⁺)-Aldrich	5.6	-	6.7	5.3
HA(H ⁺)-Aldrich	8.6	9.9/8.4	8.8	8.7
HA(H ⁺)-Gohy 573	6.3	6.3/6.4	6.9	6.1
HA(H ⁺)-Fanay-Augères	-	-	3.6	-
HA(H ⁺)-Boom Clay	6.3	-	-	-
Condition	pH = 8.5 I = 0.1	pH = 8.5/5.5 I = 0.1	pH = 8 I = 0.1	0.05 M NaHCO ₃

on pH but has no direct relation to the relative concentration of condensed rings [Chen et al. 1977]. Due to such contradictions in the literature, The E4/E6 ratio is of limited value for the characterization of humic acids.

The E4/E6 ratios measured by four different laboratories are shown in Table 17. The values for HA(H⁺)-Aldrich and HA(H⁺)-Gohy 573 are in reasonably good accord with one another, whereas the values for HA(Na⁺)-Aldrich do not agree so well. Since the absorption of humic acid at 665 nm is in general very low, the base line fluctuation of a given spectrometer contributes a substantial error to the ratio. Therefore, the accuracy of the ratio is directly related to the precision of the spectrometer. E4/E6 ratios for HA(H⁺)-Fanay-Augères and HA(H⁺)-Boom Clay are available only one value for each for the moment.

< IR-Spectrum >

IR spectroscopy of humic acid provides information on particular bond stretches at the following frequencies: 3400 cm⁻¹ for OH, 2900 cm⁻¹ for aliphatic C-H, 1725 cm⁻¹ for ketonic C=O, 1630 cm⁻¹ for aromatic C=C, C=O of carbonyl of COO⁻ or quinone, 1450 cm⁻¹ for aliphatic C-H, 1400 cm⁻¹ for aliphatic COO⁻, 1200 cm⁻¹ for C-O stretch of COOH and 1050 cm⁻¹ for Si-O impurities [Stevenson 1982]. While IR spectra of humic acids provide worthwhile information on the distribution of functional groups,

they tell little about the chemical structure of humic acids. Thus IR spectroscopy is useful only for the gross characterization of humic acids of diverse origins, and for the evaluation of the effects of different extraction processes, chemical modifications, such as methylation, acetylation, saponification and the formation of derivatives [McCathy and Rice 1985]. IR spectra of the humic acids recorded by TUM, JRC-Ispra, CEA-FAR and BGS are comparable with one another. IR spectra of HA(H⁺)-Aldrich and HA(H⁺)-Gohy 573 are quite similar, while that of HA(Na⁺)-Aldrich is, as expected from its salt form, differs substantially from the two others. The interpretation of the IR spectra will be given in a separate report that deals with exclusively the interlaboratory comparison exercise for the characterization of humic acids.

< NMR spectroscopy >

NMR spectroscopy is expected to provide more definite information on humic acids, as to their functional groups, than all other methods combined [Wershaw 1985]. At the present time the measurement of functional group concentrations in humic acids by both ¹³C and ¹H NMR spectroscopy in liquid and solid samples is at best qualitative [Stevenson 1982].

Solid state ¹³C-NMR has been carried out in cooperation with Florida State University (G.R. Choppin) for HA(H⁺)-Aldrich and HA(H⁺)-Gohy 573, including the methylated form of HA(H⁺)-Gohy 573 and the Gorleben fulvic acid: FA(H⁺)-Gohy 573 for the comparison purpose. HA(H⁺)-Boom-Clay will be included in the future report. Due to the presence of paramagnetic radicals in humic acids, the peaks can be shifted, and become significantly broader and smeared out in comparison with ordinary organic substances. Apart from the omnipresent organic radicals, inorganic paramagnetic impurities, e.g. Fe, enhances this influence as well [Wershaw 1985].

For the purified humic acids, the relative peak areas of various classes of functional groups are listed in Table 18. The ¹³C-NMR spectra are dominated by aliphatic (0-50 ppm), aromatic (108-165) and carboxylic groups (165-190) with a minor contribution of ethers, alcohols, carbohydrates and amines (50-96 ppm). The relative ¹³C-NMR peak areas, used for identi-

Table 18. Relative ^{13}C -NMR peak areas (%) of various organic components in humic acids.

Sample	Region (ppm relative to TMS):			
	Aliphatic 0-50 ppm	Ether, Alcohol, Carbohydrate, Amine 50-96 ppm	Aromatic Olefin 108-165 ppm	Carboxylate Carbonyl 165-190 ppm
HA(H ⁺)-Aldrich	41	5	40	14
HA(H ⁺)-Cohy-573(I+II)	38	8	41	13
HA(H ⁺)-Cohy-573: methylated	50 (37)	8 (10)	31 (39)	11 (14)
FA(H ⁺)-Cohy 573	48	13	23	16

(): Values corrected for methyl groups added by methylation; these values are to compare with those of non-methylated HA(H⁺)-Cohy-573.

fication of qualitative changes in structural groups, allow to a certain extent semi-quantitative conclusions.

As expected, HA(H⁺)-Gohy-573 I and HA(H⁺)-Gohy-573 II, which are separated from the same Gorleben groundwater but in the different time span, show identical results. Upon methylation an increase of aliphatic groups is observed. If the methylgroups added by methylation are corrected, almost identical spectra are attained for the humic acids with and without methylation. The fulvic acid from Gorleben is found to contain more aliphatic and less aromatic groups than the humic acid from the same groundwater. Furthermore, this fulvic acid contains somewhat larger amounts of oxygen bound groups than the two humic acids under discussion. The ¹³C-NMR features of HA(H⁺)-Aldrich resembles very much to those of HA(H⁺)-Gohy 573 same as the case for elemental compositions shown in Table 7. Therefore, a common type of origin may be postulated. Distinctive differences of NMR spectra are expected for HA(H⁺)-Fanay-Augeres and HA(H⁺)-Boom Clay whose elemental compositions are much different from both HA(H⁺)-Aldrich and HA(H⁺)-Gohy 573.

(VI) Size distribution

The molecular size of humic acids is the major important physical parameter for the migration study of radionuclide in natural aquifer systems [Kim 1986; Kim et al. 1986 b]. Complexation properties of humic acid with certain radionuclides become important if such a complex molecule will be transported along with water movement in a given aquifer system [Choppin 1988]. Knowledge of the size distribution of aquatic humic acids is, for this reason, prerequisite for the migration modeling of humate complexes.

The size distribution of aquatic humic acids can be determined by a number of physical fractionation methods, such as gel permeation chromatography, ultrafiltration, ultracentrifugation etc. [Wershaw and Aiken 1985]. Since humic acid is a polyelectrolyte, its aquatic molecular size varies with pH and ionic strength of the solution [Moulin et al. 1987 b]. Because of operational difficulties, e.g. aggregation of molecules, a careful interpretation of results is required for gel permeation chromatography and ultracentrifugation, more than for ultrafiltration.

Table 19. Molecular size distribution determined by ultrafiltration at pH 8.5: relative amount of retention on filter (in %)

HA(Na ⁺)-Aldrich				
Filter pore size	TUM	JRC-Ispra	CEA-FAR	BCS
15 nm (3 x 10 ⁵ D)	7.3 ± 0.6	-	-	-
5 nm (1 x 10 ⁵ D)	25.0 ± 2.0	9.1	-	-
3 nm (5 x 10 ⁴ D)	46.0 ± 1.0	-	-	-
2.1 nm (3 x 10 ⁴ D)	59.7 ± 2.5	32	-	46.4
1.5 nm (1 x 10 ⁴ D)	76.7 ± 2.1	56	-	66.9
1.3 nm (5 x 10 ³ D)	83.0 ± 2.0	-	-	-
1 nm (1 x 10 ³ D)	94.3 ± 0.6	-	-	95.1
<1 nm (5 x 10 ² D)	96.7 ± 0.6	99	-	-
HA(H ⁺)-Aldrich				
Filter pore size	TUM	JRC-Ispra	CEA-FAR	BCS
15 nm (3 x 10 ⁵ D)	5.0 ± 1.0	-	4.9 ± 1.0	-
5 nm (1 x 10 ⁵ D)	10.3 ± 0.6	7.9	-	-
3 nm (5 x 10 ⁴ D)	31.0 ± 0.1	7.4	14.0 ± 6.9	-
2.1 nm (3 x 10 ⁴ D)	54.7 ± 1.5	14	-	59.3
1.5 nm (1 x 10 ⁴ D)	73.7 ± 1.5	53	68.9 ± 6.2	81.2
1.3 nm (5 x 10 ³ D)	85.3 ± 1.5	-	-	-
1 nm (1 x 10 ³ D)	94.7 ± 0.6	-	92.2	96.4
<1 nm (5 x 10 ² D)	100.0 ± 1.0	97	-	99.9
HA(H ⁺)-Cohy 573				
Filter pore size	TUM	JRC-Ispra	CEA-FAR	BCS
15 nm (3 x 10 ⁵ D)	2.7 ± 0.6	-	6.4	-
5 nm (1 x 10 ⁵ D)	8.7 ± 1.2	2.7	-	-
3 nm (5 x 10 ⁴ D)	27 ± 0.1	-	31	-
2.1 nm (3 x 10 ⁴ D)	66.3 ± 1.5	36	-	53.7
1.5 nm (1 x 10 ⁴ D)	85.0 ± 1.0	61	82	76.6
1.3 nm (5 x 10 ³ D)	91.0 ± 1.0	-	-	-
1 nm (1 x 10 ³ D)	97.0 ± 1.0	-	97	96.7
<1 nm (5 x 10 ² D)	100.0 ± 0.5	99	-	100.0

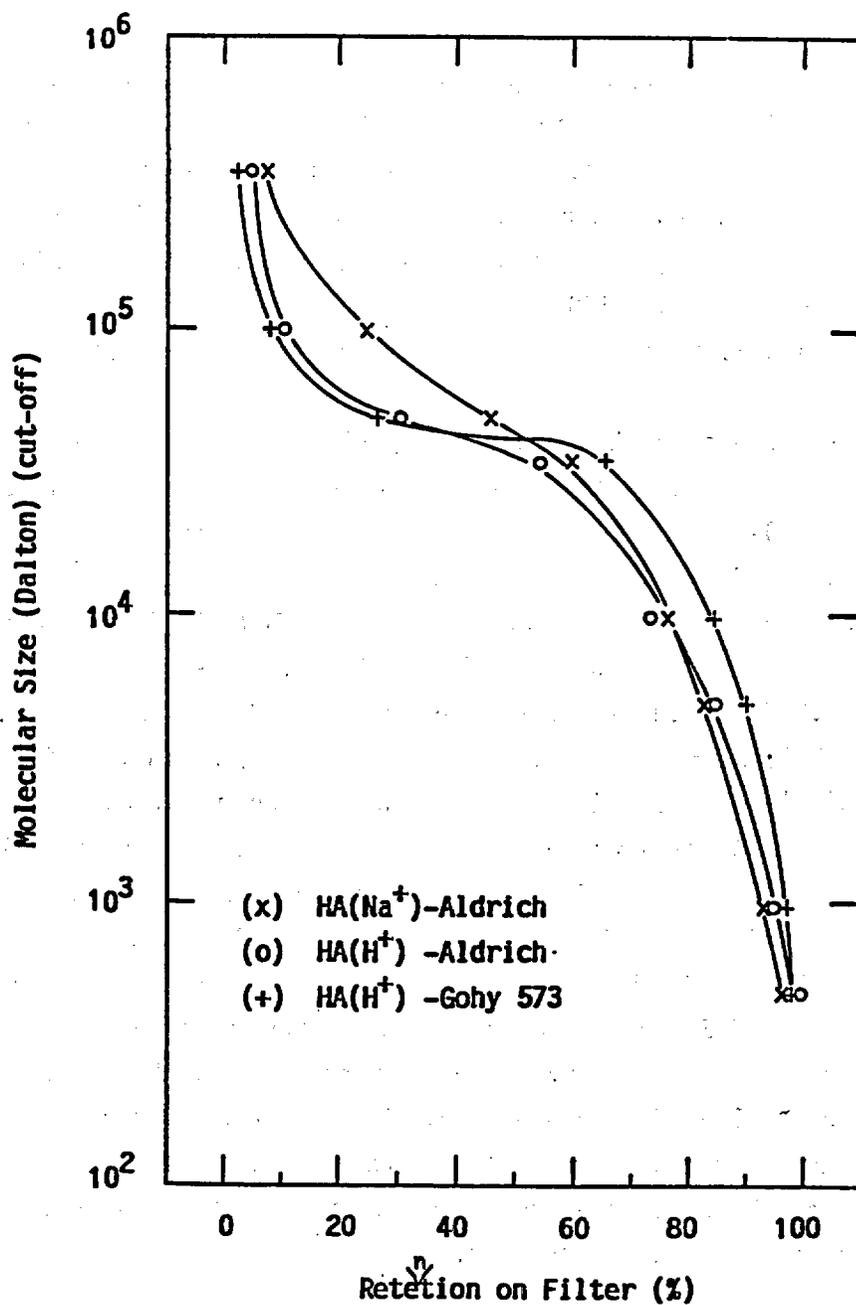


Fig. 1. Molecular size distributions of the three humic acids, used for the CEC interlaboratory comparison exercise, determined by ultrafiltration.

The size fractionation data from ultrafiltration by four laboratories are summarized in Table 19 for HA(H⁺)-Aldrich, HA(H⁺)-Aldrich and HA(H⁺)-Gohy 573. Because of the limited selection of pore sizes, except at TUM, the interlaboratory comparison cannot be realized satisfactorily. The results from TUM [Kim and Buckau 1988] for the three humic acids are shown in fig. 1, where the molecular size is plotted as a function of the relative retention amount. Based on this distribution pattern the presence of two size groups is recognized, one at about 8,000 Dalton and the other at about > 100,000 Dalton. Size differences among three humic acids are not apparent from these ultrafiltration results.

Gel permeation chromatography (GPC) has been applied by CEA-FAR [Moulin et al. 1987 b] with Shodex S-804, TUM [Kim and Buckau 1988] with Sephadex 100-120 and L-60-120, Univ. Nantes [Pieri 1989] with Sephacryl S-300; and UKAEA-chem.I [Ewart et al. 1989] with Sepharose CL-6B. The results from CEA-FAR show about 10 % of over 100,000 Dalton and 90 % of 10,000 Dalton for all three humic acids. TUM has found about 10 % of over 100,000 Dalton for the three humic acids and 90 % of 8,200 Dalton for HA(Na⁺)-Aldrich, 8,000 Dalton for HA(H⁺)-Aldrich and 9,100 Dalton for HA(H⁺)-Gohy 573. Univ. Nantes has found an average of 7000 Dalton for HA(Na⁺)-Aldrich which is in close agreement with the values obtained by CEA-FAR and TUM. UKAEA-Chem. determined much lower molecular size: 2400-2700 Dalton for HA(Na⁺)-Aldrich. HA(H⁺)-Boom Clay has been also studied by GPC at UKAEA-chem.I [Ewart et al. 1989] and Univ. Nantes [Pieri 1989]. UKAEA-chem.I found two size groups: large one around 57000 Dalton and smaller one around 4900 Dalton, while Univ. Nantes determines a large value of 123000 Dalton. These values are derived at the maximum of a broad elution peak and therefore represent an approximate average size. The results of gel permeation chromatography are in agreement with those from ultrafiltration.

Ultracentrifugation process monitoring sedimentation process has been applied by UKAEA-chem.I [Gardiner 1989] and Univ. Nantes [Pieri 1989]. The values found for HA(Na⁺)-Aldrich are 4000 Dalton by UKAEA-chem.I and 27000-107000 Dalton by Univ. Nantes. For HA(H⁺)-Boom Clay Univ. Nantes determined a size of 54000 Dalton.

All results available for the size of different humic acids estimated by various methods are summarized in Table 20. Any discussion on the results is premature for the moment before understanding the analytical process of each applied system and the condition in which each operation is pursued. Humic acid has a dynamic size which is directly affected by its hydration condition and interactions with cations in a given system. For this reason the size changes as a function of the ionic strength and pH as well as its complexation state.

Because of its importance to migration modeling, the work on size fractionation should be pursued further to achieve a precise quantification and hence to facilitate a better understanding of migration phenomena of radionuclides in a given aquifer systems.

2.1.2 Interlaboratory comparison exercise for the complexation of radionuclides with humic acids

After the characterization of the humic acids concerned, the complexation exercise has started from the beginning of 1988. For this purpose TUM again prepared and distributed HA(H⁺)-Gohy 573 (1 g each) to the participating laboratories (JRC-Ispra, RISØ, KUL, CEA-FAR, BGS, UKAEA-Chem.II, ENRESA, U.Linköping, AECL). Only Eu³⁺ and Am³⁺ ions are to be investigated in this complexation exercise.

Thus far, KUL [Cremers et al. 1987], CEA-FAR [Moulin 1989], TUM [Kim and Buckau 1989] and RISØ, [Carlsen 1989] have started the complexation study of Eu³⁺ and Am³⁺ with the reference and site-specific humic acids. JRC-Ispra [Bidoglio 1989] has studied the complexation of Eu³⁺ with fulvic acid from Bersbo, Sweden. The method used by KUL is based on an anion exchange process in carbonate solution using a resinous exchanger. By measuring anion exchange constants of Eu in the carbonate solution (Kd°) and in the same solution with addition of humic acid (Kd), the following relation is derived for a 1 : 1 Eu humate complexation with the stability constant β_H :

$$\log (Kd^\circ/Kd - 1) = \log \beta_H + \log L + \log A$$

Table 20. Molecular sizes (Dalton) determined by various methods for reference and site-specific humic acids chosen for the intercomparison exercise

Humic Acid	CEA-FAR	TUM	UKAEA-Chem I	U. Nantes	UKAEA-Chem II
HA(Na ⁺)-Aldrich	10.000 (90%)/GPC) 100.000 (10%)/GPC	8200 ± 500 (90%)/GPC) 100.000 (10%)/GPC	2600 ± 100/GPC 4000/UC	27000 - 107000/UC 7000/GPC	50 ~ 200 nm/PCS
HA(H ⁺)-Aldrich	10.000 (90%)/GPC) 100.000 (10%)/GPC	8000 ± 500 (90%)/GPC) 100.000 (10%)/GPC	-	-	-
HA(H ⁺)-Cohy 573	10.000 (90%)/GPC) 100.000 (10%)/GPC	9100 ± 500 (90%)/GPC) 100.000 (10%)/GPC	-	-	50 ~ 200 nm/PCS
HA(H ⁺)-Fanay-Augères	-	-	-	-	50 ~ 200 nm/PCS
HA(H ⁺)-Boom Clay	-	12000 ± 1000 (UF)	4900/GPC 57000/GPC	54000/UC 123000/GPC	-

GPC: Gel Permeation Chromatography; UC: Ultracentrifugation; UF: Ultrafiltration; PCS: Photon Correlation Spectroscopy.

where L is the free humic acid concentration, considered as monomeric ligand, and A comprises all thermodynamic processes for Eu hydration reactions and carbonate complexation involved in the system. The thermodynamic data for these reactions are taken from the literature. From this experiment, KUL has obtained the results as shown in Table 21 at ionic strengths of 0.01 - 0.1 M; pH=6 and pH=9.

Table 21. Complexation constants of Eu^{3+} for different humic acids

Humic acids	$\log \beta_H$ (pH = 6)(L/Eq) [Creemers 1987]	$\log \beta_H$ (pH = 9)(L/Eq) [Creemers 1989]
HA(Na^+)-Aldrich	7.7 ± 0.2	13.5 ± 0.1
HA(H^+)-Aldrich	7.6 ± 0.3	13.1 ± 0.3
HA(H^+)-Gohy 573	7.9 ± 0.3	13.0 ± 0.1
HA(H^+)-Boom Clay	7.6 ± 0.3	13.5 ± 0.2

The accuracy of these constants is directly related to the accuracy of the value A in the above equation. The difference in stability constants at the two pH values is very large, as explained by conformational changes of humic acid molecules in different pH. Humate complexation of metal ions is a function of the degree of proton dissociation, and therefore also of pH, in a given solution. The pH dependencies of the stability constants for some actinide ions from the literature [Choppin 1988] are given in fig. 2 in which bidentate complexation constants (β_2) are also included. Whether or not the increase of β values continues to the same extent beyond pH = 7 is unclear. With an increase of pH (>7) the functional groups of humic acid become deprotonated due to the lower proton concentration, so that all exchange sites become open to interactions with metal ions. This situation may give rise to a pH-independent stability constant. However, if hydrolysis reactions of metal ions are associated with their humate complexation, then the interaction behaviour of metal ions with humic acid could be dependent on the pH. This may be an explanation for the results obtained by KUL where β changes with pH even at the higher pH (>7).

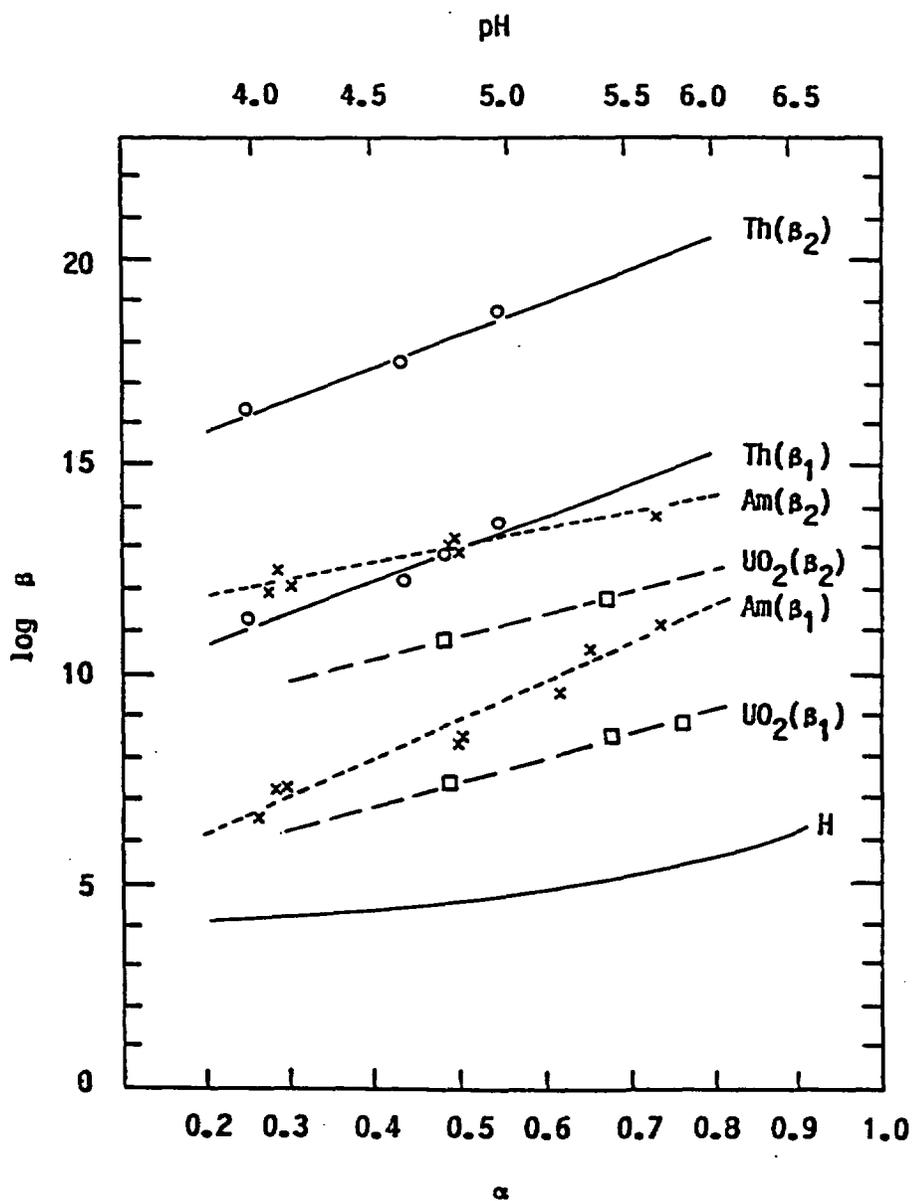


Fig. 2. Stability constants of humate complexes of some actinides as a function of the degree of dissociation (HA) and of pH. (G.R. Choppin, "Migration 87", Radiochimica Acta)

Spectroscopic as well as chromatographic studies of Am-humate complexation have been undertaken by CEA-FAR [Moulin 1987a and 1989] for Am solutions of $(2.5-3.1) \times 10^{-5}$ mol/L and 10^{-7} mol/L, respectively, in 0.1M NaClO₄ at pH = 4.65 with addition of 0.005M or 0.0025M NaAc. The humic acid concentration is varied between 0 and 60 mg/L for the spectroscopic study, whereas in the chromatographic experiment the humic acid concentration is maintained at 0.5 g/L. Complexation constants of the 1:1 interaction for humic acids are given in Table 22.

Table 22. Complexation constants of Am³⁺ for different humic acids [Moulin et al. 1987 a; 1989]

Humic acid	log β (pH=4.65) (L/Eq)	
	Spectroscopy	Chromatography
HA(H ⁺)-Bersbo	7.0 ± 0.2	-
HA(H ⁺)-Bradford	7.0 ± 0.3	-
HA(Na ⁺)-Aldrich	-	7.5 / 7.4
HA(H ⁺)-Aldrich	7.5	7.0 / 7.1
HA(H ⁺)-Gohy 573	-	7.2 / 7.4
HA(H ⁺)-Fanay-Augères	-	6.8 / 7.3

RISØ [Carlsen 1989] has studied the complexation of Eu³⁺ with the reference as well as site-specific humic acids, using the ion exchange method (Dowex 50 (Na⁺)) in 0.1M NaCl at pH=6.0. The results calculated in L/Eq. unit based on the original data in L/g unit, using the proton exchange capacities of 5.43 eq./g for HA(Na⁺)-Aldrich and HA(H⁺)-Aldrich, 5.38 eq./g for HA(H⁺)-Gohy 573, 3.4 eq./g for HA(H⁺)-Fanay-Augères are summarized in Table 23.

The humic acid: HA(H⁺)-Fanay-Augères is a product before final purification. These results are comparable with those determined by KUL at the same pH. Since the values from CEA-FAR are determined at pH=4.65, they are not directly comparable with the values from RISØ, though both sets of data appear to be similar.

Table 23. Complexation constants of Eu^{3+} for different humic acids [Carlsen 1989]

Humic acid	$\log \beta$ (pH=6.0) (L/Eq)
HA(Na^+)-Aldrich	7.4 ± 0.2 (3)
HA(H^+)-Aldrich	7.6 ± 0.1 (3)
HA(H^+)-Gohy 573	7.7 ± 0.4 (22)
HA(H^+)-Fanay-Augères (unpurified)	4.4 ± 0.8 (6)

(): number of determinations

TUM has used different methods, i.e. Laser-induced photoacoustic Spectroscopy, UV-spectroscopy and ultrafiltration for the complexation study of Am^{3+} . In this study TUM [Kim and Buckau 1989] has found that the complexation constant, being independent of pH and ionic strength, can be determined when the loading capacity of humic acid for the metal ion in question is known. The loading capacity is a function of pH and ionic strength, increasing with pH increase and with decrease of ionic strength. Furthermore it is found that the Am^{3+} ion undergoes "tridentate" complexation with the functional groups of humic acid when the concentration ratio of humic acid to Am^{3+} is very large. Experimental results are summarized in Table 24, in which the complexation constants independent of pH and ionic strength are given together with experimental conditions.

JRC-Ispra [Bidoglio 1989] has introduced Time Resolved Laser Fluorescence Spectroscopy (TRLF) for the complexation study of Eu^{3+} with Bersbo fulvic acid: FA(H^+)-Bersbo. The ionic strength is maintained constant at 0.1M and 1.0M NaClO_4 while pH is varied from 2.7 to 6.5. The binding capacity of Eu^{3+} (mmol Eu/g), which may be compared with the loading capacity described by TUM, is found to be increasing with pH increase. The complexation constants determined by taking account of the binding capacity appear pH independent. The results are given in Table 25.

Table 24. Complexation constants of Am^{3+} for different humic acids under various experimental conditions [Kim and Buckau 1989]

Humic Acid	pH	I (M)	L	Method	Log β (L/mol)
HA(H ⁺)-Aldrich	6.0	0.1	(0.650)	LPAS	6.27 ± 0.04
HA(H ⁺)-Cohy 573	6.0	0.1	0.500	UV-Spectroscopy	6.68 ± 0.47
HA(H ⁺)-Bradford	6.0	1.0	0.518	UV-Spectroscopy	6.28 ± 0.34
HA(H ⁺)-Bradford	6.0	0.1	0.650	Ultrafiltration	6.53 ± 0.30
HA(H ⁺)-Bradford	6.0	0.1	0.650	UV-Spectroscopy	6.16 ± 0.38
HA(H ⁺)-Bradford	5.5	0.1	0.400	UV-Spectroscopy	6.42 ± 0.34
HA(H ⁺)-Bradford	5.0	0.1	0.190	UV-Spectroscopy	6.41 ± 0.70

I (M): Ionic strength of NaClO_4 ; L: Loading capacity of Am^{3+} on humic acid for each given condition; LPAS: Laser-induced Photo-acoustic Spectroscopy.

Table 25. Complexation constants (preliminary results) of Eu^{3+} for the Bersbo fulvic acid [Bidoglio 1989]

pH/l(M)	Binding capacity (mmol Eu/g)	log β (L/mol)
2.7 / 0.1	~ 0.5	6
5.5 / 0.1	0.78 ± 0.04	5.90 ± 0.05
6.5 / 0.1	1.30 ± 0.05	6.00 ± 0.09
2.7 / 1.0	~ 0.5	6
5.5 / 1.0	0.91 ± 0.04	6.00 ± 0.1
6.5 / 1.0	0.63 ± 0.05	6.50 ± 0.15

2.2 Colloid generation in groundwater

Colloids have been identified as potentially important in the migration of the actinides and some fission products in aquifer systems [Avogadro and de Marsily 1984; Kim et al. 1984; Buckau et al. 1985; Kim 1986]. They are defined as being of three kinds: real-colloids, groundwater-colloids and pseudo-colloids [Kim et al. 1984]. Real-colloids are produced by the aggregation of hydrolysed radionuclides, groundwater-colloids are ubiquitous in all aquifer systems and pseudo-colloids are generated by sorption of radionuclides on groundwater-colloids. The size of colloids under discussion is defined as being less than 0.45 μm ; these remain stably dissolved in groundwater.

Those radionuclides which tend to hydrolyse in groundwater will generate either real-colloids or pseudo-colloids [Kim 1984; Buckau et al. 1985; Kim 1986]. Nearly all actinide ions and some fission products of higher oxidation states ($Z \geq 3+$) belong to this category: the tendency is strongest with trivalent and tetravalent ions, followed by hexavalent ions, and is least with ions of pentavalent state [Kim 1986]. In near neutral solutions of low ionic strength, the generation of real-colloids of tri-, tetra- and hexavalent radionuclides is prevalent, each to a different extent. Because the solubility of these ions in such solutions is generally very low, and accordingly the concentration of real-colloids is low, quantification of real-colloid formation can often be pursued only by ultrafiltration combined with radiometric measurements. Real-colloids readily undergo interactions with groundwater-colloids to form

pseudo-colloids; a result that could significantly affect the migration process of those radionuclides [Rommel and Kim 1986].

The project MIRAGE II includes a coordinated investigation on colloids, beginning with groundwater-colloids in some site-specific aquifer systems. After preliminary screening of geochemical conditions, three groundwaters were chosen for sampling and characterization as a part of the interlaboratory comparison exercise. The selected groundwaters come from

- Markham Clinton (UK),
- Grimsel (Switzerland)
- Gorleben (F.R. Germany).

In addition to the interlaboratory comparison exercise, the generation of actinide pseudo-colloids and the characterization of humic colloids in Gorleben aquifer systems are also in progress in TUM [Kim et al. 1989] and UKAEA-Phys. [Ivanovich et al. 1989]. The colloid generation in granitic water and the behaviour of synthetic colloids, e.g. Ceria, Silica, Iron oxide, are under investigation by UKAEA-Chem.II [Ramsay 1989].

2.2.1 Interlaboratory comparison exercise on groundwater colloids

A list of participating laboratories and individual exercises is given in Table 21. First, groundwaters from three different aquifer systems: consolidated sandstone at Markham Clinton (UK), fractured granite at Grimsel (Switzerland) and glacial clays at Ispra (Italy) were examined for their suitability for the interlaboratory comparison exercise, particularly as to the colloid population of each water. The quantification of colloids made by TUM [Klenze and Kim 1986], using laser-induced photoacoustic spectroscopy (LPAS) provided the following results:

Groundwater	Colloid population	
Markham Clinton	ca. 10^9	particles/L
Grimsel	$10^9 - 10^{10}$	particles/L
Ispra	ca. 10^9	particles/L
Gorleben (Gohy-1011) (reference)	$10^{11} \sim 10^{12}$	particles/L

After this preliminary screening examination, the water from Ispra was eliminated from the exercise plan due to its low colloid population and the other two waters were considered further for the coordinated exercise. Following the completion of the interlaboratory comparison study by five laboratories [Ross et al. 1987; Longworth et al. 1989], the Markham Clinton water was no more under consideration for the future study.

A Gorleben groundwater containing a substantial amount of colloids (Gohy-214) was then proposed to include in the interlaboratory comparison exercise together with the groundwater from Grimsel. However, no enthusiastic support has been shown by the laboratories which agreed initially to carry on the exercise and then received samples (8 laboratories). For this reason a bilateral exercise between TUM and UKAEA-Phys. has been launched for the characterization of colloids in selected Gorleben groundwaters, subsequently to study the colloid migration behaviour using natural analogues (Th, U).

The colloid characterization study carried out hitherto in the framework of the interlaboratory comparison exercise is summarized briefly.

(I) Markham Clinton groundwater [Ross et al. 1987; Longworth et al. 1989]

The exercise with this water was joined by BGS (host lab.), JRC-Ispra, CEA-FAR, PSI and UKAEA-phys. The Markham Clinton aquifer is presently used for the public water supply for Nottingham, with a complex of three boreholes abstracting groundwater at a rate of approximately 10^6 L/h. Colloid sampling is carried out by collecting two types of samples: a cross flow filtration on membrane filters and a diafiltration to produce aqueous colloid concentrates.

The colloid population on the filter samples was estimated by four laboratories, BGS, CEA-FAR, UKAEA-Phys. and PSI, using scanning electron-microscopy (SEM). By measuring individual particle sizes and converting them to a sphere diameter of equivalent area, a size distribution was obtained by summing particle numbers of equivalent diameter over a total area measured. Artifacts, such as the bacteria and membrane defects, were

eliminated manually from the particle count. The results from four different laboratories are summarized in Table 26.

Table 26. Colloid population in Markham Clinton Groundwater determined by SEM

Sample Phase I+II	BCS	PSI	CEA-FAR	UKAEA-Phys.
Area anal. (μm^2)	900 - 20.000	1.600 - 3.240	~ 1.000	1.000 - 2.400
Lower limit (nm)	50	40	100	80
Particles/L	$(0.6-2.5) \times 10^8$	$(0.4-2.0) \times 10^8$	1×10^6	$(2-4) \times 10^8$

Filter pore size: 10.000 Dalton (ca. 1.5 nm); Sample water: 100 - 220 mL

The grand average of the values in Table 26 is further compared with the results obtained by other methods as shown in Table 27.

Table 27. Comparison of colloid populations in Markham Clinton groundwater determined by different methods

SEM	SLS	LPAS
$(1.2 \pm 0.5) \times 10^8$) 40 nm	$(0.7 \pm 0.3) \times 10^8$) 500 nm	ca. 10^9 -

SEM: Scanning Electron Microscope; SLS: Static Light Scattering [UKAEA-Phys.]; LPAS: Laser-induced Photoacoustic Spectroscopy [TUM]

Generally it is considered that the SEM counts underestimate the total colloid population due to the limitation imposed by SEM resolution (>50 nm) as well as the aggregation of colloids in the sample preparation. Whether the data in Table 27 represent approximately the real population of colloids is difficult to be verified, since there is no straightforward method to count colloids of polydispersive sizes in such low concentrations.

The particle population is even more difficult to characterize in the aqueous colloid concentrate. JRC-Ispra and UKAEA-Chem.II both have attempted to determine the particle size distribution directly in the colloid concentrate using photon correlation spectroscopy. In both cases the colloid population proved to be too low to provide a reliable interpretation of spectra. The UKAEA-Chem.II data, indicating an hydrodynamic radius of 9.7 μm , suggests that the aggregation might have occurred.

Elemental analyses of groundwater, colloid concentrate and ultrafiltrate by BGS, JRC-Ispra and UKAEA-Phys. are in good agreement with one another. All samples show the same composition of major elements: Ca, Mg, Na, K, Si; Cl^- , SO_4^{2-} , HCO_3^- . The colloids, analysed by SEM-EDX, contain Ca, Si, Al, Mg, K, Na, Mn, Fe and Zn.

As a result of this exercise carried out during 1987 and 1988, the following conclusions and recommendations for future work can be made: (1) Cross flow membrane ultrafiltration provides reproducible colloid samples which are relatively easy to enumerate by analysis of SEM micrographs. The present resolution of ~ 50 nm obtainable with SEM places a restriction on the size of colloid particles which can be distinguished. (2) Good agreement has been obtained for colloid populations ($10^8 - 10^9$ particles/litre) obtained by SEM and LPAS. The latter technique is non-invasive but is a less direct method than SEM, relying at present on calibration against model colloids. (3) Samples produced by tangential flow ultrafiltration can be used to determine the natural actinide loadings on the colloid phase. For Markham Clinton groundwater these are several percent for thorium isotopes but less than 0.1 % for uranium, of the total groundwater activity. (4) Possible losses of colloids during the preparation of an aqueous colloid concentrate, together with aggregation effects require further investigation. (5) Photon correlation spectroscopy at present is not able to provide the colloid size distribution but further development would be useful.

(II) Grimsel groundwater [Degeldre 1987; 1988 a]

The groundwater from the Felslabor Grimsel (Switzerland) flows from a mylonitic fracture zone within a granodiorite body and contains colloids

of organic and inorganic origin. The colloid population counted by the SEM micrograph technique, after diaultrafiltration of the water is given in the range of $(2 \sim 4) \times 10^{10}$ particles/L, which is in the close proximity to the first value measured at TUM ($10^9 \sim 10^{10}$ particles/L) directly in the solution by LPAS [Klenze and Kim 1986].

The interlaboratory comparison exercise for the Grimsel water was intended primarily to test the in-situ sampling of aqueous colloids and thereafter to characterize them. This exercise was joined by PSI (host lab.), JRC-Ispra, CEA-FAR, UKAEA-Chem.II, BGS and AECL. Progress in this work was reported by Degueldre separately [Degueldre et al. 1988 a].

The colloid concentrate filtered on the Amicon-XM50 (3 μ m pore size) together with the original groundwater sent to TUM were analysed by SEM and LPAS, respectively. The colloid population counted at TUM by the two methods are:

SEM:	$(0.6 - 1.5) \times 10^9$	particles/L	(> 50 nm)
LPAS:	4.2×10^{11}	particles/L	

For the LPAS measurement an average size is assumed to be 100 nm, which is based on the size distribution spectrum obtained at TUM by SEM. The present value is larger than the previous value ($10^9 \sim 10^{10}$), because of an average size assumed in the former measurement being 200 nm. At that moment the size distribution of colloids in Grimsel water was unknown.

(III) Gorleben groundwater

The Gorleben aquifer system overlying a salt dome is composed of a variety of hydrogeological and geological formations, which are characterized as porous sediments in part mixed with clay zones. Analyses of over 100 different groundwaters indicate the presence of dissolved organic carbons (DOC) ranging from 0.1 mgC/L to nearly 100 mgC/L [Kim et al. 1986a and 1986b]. Colloids are also abundant, and are composed of inorganics as well as organometallic composites [Buckau et al. 1985]. The latter colloids are made of humic acid loaded by metal ions and behave like a soluble ion exchanger [Kim et al. 1987].

One of Gorleben groundwaters has been chosen for the interlaboratory comparison exercise for colloid population counting and composition analysis. For this purpose the groundwater (Gohy-214), in contact with the original sediment, was distributed to the members of the COCO club. The sediment contact is necessary to preserve geochemical equilibria of colloids in groundwater during the transportation and storage. Preliminary analytical data for the water containing colloids included in the distribution are expected to help to control the eventual changes occurring in the course of time.

The colloid populations determined using SEM micrographs at PSI, UKAEA-Phys., BGS [Degueldre 1988 b; Williams et al., 1989; Longworth and Ivanovich 1988], Static Light Scattering (SLS) at UKAEA-phys. [Longworth and Ivanovich 1988] and LPAS at TUM are summarized in Table 28.

Table 28. Colloid populations in Gorleben groundwater (Gohy-214) determined at different laboratories using various technique

Laboratory	Low limit	Colloid population	Method
PSI	> 40 nm	$(5.7 \pm 1.0) \times 10^9$ particles/L	SEM
UKAEA-Phys.	> 80 nm	$(1.8 \pm 0.2) \times 10^9$ particles/L	SEM
UKAEA-Phys.	> 500 nm	$(1.1 \pm 0.3) \times 10^8$ particles/L	SLS
BGS	> 50 nm	$(2.1 \pm 1.4) \times 10^{10}$ particles/L	SEM
TUM	-	$(3.6 \pm 0.2) \times 10^{12}$ particles/L	LPAS

The DOC concentration in this groundwater was found to be 5 mgC/L which corresponds to ca. 10 mg/L humic acid. With this amount of humic acid, the groundwater colloids are organic in nature, i.e. humic acid loaded with metal ions. The population estimation for such colloids is a new challenge, since they are sensitive to aggregation on filtration and it is therefore difficult to identify the original sizes of the particles. As humic colloids are in general smaller in size, i.e. $\ll 100$ nm, the SEM micrograph counting of original particles is limited by resolution. The colloid populations counted by SEM and SLS are certainly underestimated.

(IV) Bilateral comparison exercise (TUM and UKAEA-Phys.)

The main objective of this feasibility study is to establish a possibility of evaluating colloid migration in natural aquifer systems. Since the Gorleben aquifer consists of porous sediments in part mixed with clays and contains much of natural organometallic colloids, the study of colloid migration in such an aquifer can be realized more easily than in any other aquifer. As indicators to trace colloid migration, the natural analogue elements, i.e. Th and U isotopes, are chosen to follow their geochemical behaviour.

Sampling and characterization of colloids and groundwaters from a selected hydrological pathway have been organized by UKAEA-Phys. and TUM. Two boreholes (Gohy-1231 and Gohy-2227) are selected, in which groundwaters are known to be rich and poor in humic colloids and one of them is saline. The geochemical characterization is in progress for the moment for the two borehole samples. The preliminary results of U and Th isotopic partition between colloids and groundwaters are given in Table 29 [Ivanovich et al. 1989; Kim et al. 1989].

The Gohy-1231 water is saline (492 meq/L salt) containing 3.6 mg C/L of DOC, whereas the other sample: Gohy-2227 contains much higher concentration of DOC (88.6 mg C/L) but nonsaline (85 meq./L salt). The later contains much of organometallic colloids which contain the major part of U and Th isotopes. A contrary phenomenon is observed in Gohy-2131 which contains lower amount of colloids and U and Th isotopes are found accordingly in the liquid phase.

2.3 Basic retention mechanisms

This subject comprises a number of research projects at different laboratories in the CEC member countries, started in the second phase of the project MIRAGE II. All those new projects commenced in 1988 together with some of on-going projects are coordinated in the framework of the COCO club activities. The coordination should result in a well consolidated program for generating mutually beneficial results among the participating laboratories, as has been the case for the previous common activi-

Table 29. U and Th isotopic partition (%) in Gorleben groundwaters: Gohy-1231 and Gohy-2227

Parameter	Gohy-1231		Gohy-2227	
Color	clear		brown	
pH	7.01		7.73	
Eh (mV)	273.2		- 66.2	
Salt (meq/L)	492		85	
DOC (mg C/L)	3.6		88.6	

Isotope	Colloid (>1.5 nm)		Filtrate	
U-238	2	98	89	11
U-234	0.5	99.5	85	15
Th-232	3	97	94	6
Th-230	1	99	85	15
Th-228	1	99	68	32

ties in the COCO club. The subject is subdivided into a number of research themes which are enumerated as follows:

- Influence of natural organics and colloid generation on the chemical behaviour of radionuclides in the near and far field
- General retention processes in the sorption experiment
- Speciation of radionuclides in the geochemical environment
- Compilation and evaluation of thermodynamic data relevant to the elucidation of migration phenomena
- Theoretical prediction of sorption phenomena: modeling of the laboratory sorption process

2.3.1 Influence of natural organics and colloids generation on the chemical behaviour of radionuclides in the near and far field

The influence of natural organics on the solubility and retention process of actinides and some fission products is, as expected, an obvious phenomenon, of which the underlying process need to be understood more clearly. A number of investigations has been undertaken at different laboratories to characterize the influence of humic acids and other organics, i.e. on the solubility of ^{241}Am [Ewart et al. 1989]; on the diffusion and sorption of ^{36}Cl and ^{237}Np in clay matrix [Staunton et al. 1989]; on the sorption of ^{60}Co on sediments of glacial sand [Warwick et al. 1989]; on the ^{238}Pu sorption on the Mol sand. Since much of these works is still in progress, some of preliminary results are summarized in this review report.

(I) Influence of humic acid on the solubility of Am(III) [Ewart et al. 1989]

The solubility of Am has been studied at high pH (12.7) in solutions of humic acid extracted from Boom Clay in contact with water equilibrated with a 9:1 Blast Furnace Slag: ordinary Portland cement (BFS/OPC) grout.

Table 30. Am concentrations in NaOH extracts and 9 : 1 BF/OPC extracts of Boom Clay humic acid [Ewart et al. 1989]

[HA] (mg/L)	[Am]-Inventory (mol/L)	Am concentration (mol/L) in filtrates of	
		30.000 Dalton (2.1 nm)	450 nm
in NaOH extracts			
240	4.1×10^{-8}	9.1×10^{-10}	3.8×10^{-8}
24	4.1×10^{-8}	2.5×10^{-9}	3.8×10^{-8}
2.4	4.1×10^{-8}	4.5×10^{-9}	3.7×10^{-8}
0	4.1×10^{-8}	2.7×10^{-9}	3.4×10^{-8}
240	4.1×10^{-6}	1.0×10^{-8}	3.8×10^{-6}
24	4.1×10^{-6}	3.8×10^{-9}	3.9×10^{-6}
2.4	4.1×10^{-6}	1.4×10^{-9}	3.5×10^{-6}
0	4.1×10^{-6}	9.2×10^{-12}	2.1×10^{-9}
in BFC/OPC extracts			
13	4.1×10^{-8}	7.4×10^{-11}	3.1×10^{-8}
1.3	4.1×10^{-8}	1.4×10^{-10}	4.0×10^{-9}
0.13	4.1×10^{-8}	1.7×10^{-10}	8.3×10^{-12}
0	4.1×10^{-8}	4.1×10^{-11}	1.7×10^{-10}

BFC/OPC: Portland cement

The initial experiment was carried out in solution before its contact with the cement, introducing two different Am concentrations: 4.1×10^{-6} mol/L and 4.1×10^{-8} mol/L Am. All operations were carried out in a N₂ flushed glove box. From these experiments the potential for increased Am solubilities can be observed. The effects may be lessened by competition for complexation sites by other inactive ions, e.g. Ca²⁺, which may also decrease the level of soluble humic substances. The preliminary results from the solubility experiments are summarized in Table 30.

(II) Influence of natural and man-made organics on the diffusion and sorption of ³⁶Cl and ²³⁷Np [Staunton et al. 1989]

The diffusion and sorption studies of ³⁶Cl and ²³⁷Np have been carried out for Na and Ca form clays, i.e. montmorillonite, kaolinites, illite, in a perchlorate medium. The influence parameters investigated are concentrations of Na⁺, Ca²⁺, EDTA, Citrate and humic acid. The diffusion experiment of ³⁶Cl was made to calculate the impedance factor of an ion in solution, which is expected to be the same for each species in solution unless further impeded by geometric or electrostatic interactions. Sorption coefficients of ²³⁷Np (Rd: cm³/g) were evaluated from the adsorption isotherms, which were found to be linear within the investigated concentration range: 3×10^5 - 7×10^6 cpm/mL. These values, together with the impedance factor determined by ³⁶Cl, were used to calculate contributions of the liquid phase to the measured diffusion coefficient. The diffusion coefficient was measured in a cell containing two compartments inbetween the clay matrix being placed. The results are summarized in Table 31.

(III) Influence of humic acid on the Pu sorption [Bidoglio et al. 1989]

The Pu adsorption on pure β-alumina and heterogeneous mineral phases was investigated as a function of the pH and humic acid concentration. The surface redox reaction of Pu(V) appeared to control the Pu retention on electron exchanging minerals. The experiment with a clay sand column under the reducing condition (Eh ≤ -200 mV) showed that HA particles larger than 600 nm were retained in the column, while the HA break-through was characterized by an extended elution tailing. The chemical associa-

Table 31. The sorption and diffusion behaviour of ^{237}Np in different clay components under the influence of different cations and organics [Stounton et al. 1989]

Solution (mol/L)		Sorption coefficient (cm^3/g) for Np			Diffusion coefficient (m^2/S)			
		Montmorillonite	Kaolinite	Illite	Montmorillonite Np($\times 10^{-13}$)	Cl($\times 10^{-10}$)	Kaolinite Np($\times 10^{-11}$)	Cl($\times 10^{-10}$)
Na^+	10^{-3}	68.4 ± 3.4	18.4 ± 1.1	-	14.9 ± 1.5	7.1 ± 0.2	2.9 ± 0.1	4.7 ± 0.3
	10^{-2}	82.8 ± 9.9	5.0 ± 0.8	64.4 ± 15.5	11.6 ± 2.8	5.7 ± 0.1	3.6 ± 1.3	4.7 ± 0.3
	10^{-1}	79.6 ± 4.8	4.1 ± 1.1	-	15.8 ± 2.2	6.7 ± 0.7	3.0 ± 0.4	4.5 ± 0.4
Ca^{2+}	10^{-3}	143.4 ± 11.5	3.5 ± 3.3	-	4.8 ± 0.8	4.2 ± 0.3	3.0 ± 0.6	5.3 ± 1.1
	10^{-2}	81.8 ± 10.6	1.7 ± 1.1	22.0 ± 3.3	8.1 ± 0.3	5.8 ± 0.2	3.1 ± 0.1	4.9 ± 0.3
	10^{-1}	18.8 ± 2.8	1.4 ± 0.9	-	11.6 ± 1.9	5.6 ± 0.2	3.3 ± 0.8	5.1 ± 0.3
EDTA	10^{-5}	65.1 ± 7.8	0.9 ± 0.9	15.3 ± 0.9	5.9 ± 0.4	6.3 ± 1.0	8.0 ± 0.6	5.3 ± 0.3
	10^{-3}	59.3 ± 3.0	5.3 ± 1.5	12.7 ± 0.8	6.4 ± 2.4	6.8 ± 0.2	8.2 ± 1.0	5.3 ± 0.5
Citrate	10^{-5}	55.6 ± 8.9	2.1 ± 3.4	14.0 ± 1.3	4.2 ± 1.2	6.4 ± 0.6	6.2 ± 0.1	4.0 ± 0.4
	10^{-3}	77.4 ± 10.8	32.3 ± 4.5	34.1 ± 4.1	5.7 ± 1.8	$6.7 \pm$	6.0 ± 0.5	$4.1 \pm$
Humic Acid	10^{-5}	68.2 ± 6.1	3.8 ± 2.2	21.0 ± 2.9	1.1 ± 0.2	4.8 ± 0.8	1.4 ± 0.4	4.5 ± 0.2
	10^{-3}	92.0 ± 18.4	20.1 ± 5.2	36.3 ± 5.8	1.3 ± 0.4	5.5 ± 0.1	1.3 ± 0.1	4.5 ± 0.2

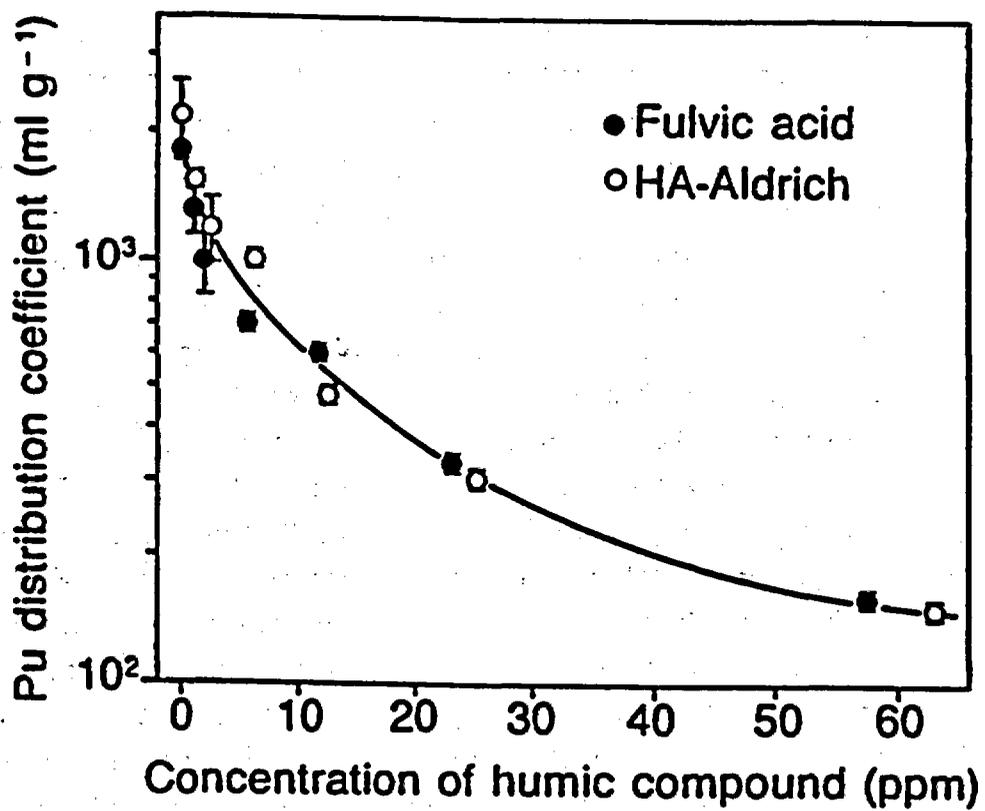


Fig. 3. Influence of solution concentration of different humic substances on the distribution coefficient for Pu on glauconitic sand under reducing conditions ($E_h \leq -200$ mV)

tion of Pu with mobile HA, investigated by leaching of a ^{238}Pu doped bore silicate glass, enhanced the Pu release rate in HA solutions in comparison with HA-free water. A representative picture of the Pu sorption behaviour as a function of the HA concentration is shown in fig. 3, which demonstrates clearly the influence of HA on the sorption of Pu.

(IV) Influence of natural and man-made organics on the mobility of ^{60}Co
[Warwick et al. 1989]

Acetate, EDTA and organic compounds naturally present in groundwater at the Drigg in situ radionuclide migration experimental site, have been studied to assess their effect on the sorption of cobalt by glacial sand in a series of batch experiments. Removing 56 % of the natural organic material from the groundwater with DEAE (diethylaminoethyl) cellulose increased the distribution ratio (Rd) of cobalt by a factor of about two. EDTA had a dramatic effect on the sorption of Co even at low concentrations reducing the Rd by up to 2 orders of magnitude. At EDTA concentrations greater than 5 mg/L, there was no further reduction in sorption. EDTA was not itself sorbed, but formed a mobile complex with Co. Differences in distribution ratios were observed dependent on whether the cobalt was added before or after EDTA. Within the same period of equilibrium, the Rd values were higher when cobalt was allowed to equilibrate with the sand before adding EDTA. The desorption of cobalt from the mineral surface may be a rate limiting step such that equilibrium was not achieved within the 14 days period of these experiments. Acetate had no effect on cobalt sorption in any of the experiments undertaken. The influence of natural organics (presumably fulvic acid) on the sorption of ^{60}Co is shown in Table 32.

Table 32. Influence of natural organics present in groundwater on the sorption of Cobalt by glacial sand [Warwick et al. 1989]

Sample	Sorption coefficient (cm^3/g)	
	natural groundwater	groundwater removed of natural organics
Co added at the beginning	140 ± 28	292 ± 12
Co added after 7 days	323 ± 51	786 ± 73

(V) Influence of humic acid on the diffusion and sorption (retention) behaviour of Tc, Np, Se and Eu in Boom Clay formations [Henrion et al. 1988]

The diffusion experiment of Tc with a preconsolidated clay plug conditioned with HA containing groundwater showed that the diffusive transport was extremely small and appeared to associate with the apparent diffusion constant found: 2×10^{-10} cm²/s, which represents the optimal reducing condition. Contrary to this, the diffusion constant of 1.4×10^{-6} cm²/s was observed in the oxidizing condition. The speciation study of Tc in the presence of humic acid has been carried out parallelly to verify the fact that in Boom Clay groundwater TcO_4^- undergoes reduction and complexation with humic acid. A Gel permeation chromatographic experiment with Sephadex-G25 demonstrated the elution behaviour of Tc that corresponds to the humic acid elution. The reduced oxidation state was presumably Tc(IV).

The batch sorption experiment of Tc with pyrite (FeS_2) has been also carried but with and without HA addition. The TcO_4^- sorption on pyrite was explained by its reduction on the mineral surface to form TcS_2 . An addition of a small amount of HA reduced sharply the Tc sorption on pyrite but did not yield a complete desorption of Tc. This phenomenon was explained by the surface sorption of HA on pyrite.

An interesting experiment carried out was the exchange of the Eu isotope between large and small HA molecules. The kinetics of such an exchange would certainly be an important parameter to explain the diffusive transport of Eu in Clay formations. The experimental finding was that the exchange kinetics were very slow. However, the experimental time was too short (10 days) to produce any valuable result.

2.3.2 General sorption experiments [Wolfrum et al. 1989]

The work designed under this subject is to examine different experimental procedures which are to quantify the retention behaviour of radionuclides in Gorleben aquifer systems. Experimental procedures under consideration are diffusion, static (e.g. batch) and dynamic (e.g. column)

processes, which are commonly used for evaluation of the retention behaviour of radionuclides. During the past short contract period, the batch sorption and diffusion experiments have been carried out for six different elements, Sr, Zr, Nb, Tc, Eu and Pu in 9 different Gorleben aquifer samples composed of porous sediments and clay components. A general feature of the results obtained hitherto indicates that Tc shows no visible retention regardless of different geomatrices, whereas Zr, Nb and Eu are well sorbed on nearly all samples: more on clay matrix than on sand, while Sr shows a moderate sorption undistinguished by geomatrix.

2.3.3 Speciation [Klenze and Kim 1988]

The speciation of actinides in natural aquifer systems is a direct way of supporting the validation of geochemical modelings as well as of thermodynamic data used for the migration study. The speciation sensitivity of actinides required for the purpose remains in the range from 10^{-6} mol/L to 10^{-11} mol/L, which is the solubility range of different actinide complexes in natural aquifer systems. Such a speciation sensitivity can be achieved by modern spectroscopic methods which provide non-perturbing speciation. TUM has installed a combined system of spectroscopy that comprises photoacoustic detection and time resolved fluorescence measurement of an absorber excited by variable laser light sources. The laser-induced photoacoustic spectroscopy (LPAS) has a speciation sensitivity as low as

$$\alpha = \epsilon C = 3 \times 10^{-6} \text{ cm}^{-1}$$

for the Am^{3+} ion. Further improvement of the LPAS sensitivity is directly limited by the water absorbance which cannot be compensated better than a factor of 10^{-2} .

The application of LPAS to the characterization of colloids has been successfully tested at TUM [Wimmer et al. 1989]. The principle of the method is based on the time resolution of the photoacoustic signal generated from the absorption and scattering of incident light. The light scattering caused by colloids in solution is monitored directly by a transducer (Piezocrystal) and the signal is correlated to the particle size and concentration. Colloid populations estimated by this technique are summarized in Table 33.

Table 33: Determination of colloid population in groundwaters by LPAS

Groundwater	P.A. Signal ($\mu\text{V/mJ}$)	Colloid content (ppm)	Population * (N/L)
Grimmel water	0.166	0.095	4.2×10^{11}
Gohy-1011	0.176	0.101	4.4×10^{11}
Gohy-214	1.445	0.830	3.6×10^{12}
Gohy-S105	3.175	1.824	8.0×10^{12}
Gohy-S104	7.645	4.393	1.9×10^{13}

*: evaluation based on the average diameter of colloids at 100 nm

The time resolved laser fluorescence spectroscopy (TRLF) installed in TUM has the speciation sensitivities as shown in Table 34. Direct speciations of actinides have been demonstrated in the sorption experiment [Klenze and Kim 1989], the Am humate complexation study [Kim and Buckau 1989] and the actinide chemistry [Klenze and Kim 1988].

Table 34. Speciation sensitivities of time resolved fluorescence spectroscopy

	Cm^{3+}	UO_2^{2+}	Am^{3+}	HA
Excitation (nm)	398	308	503	360
Emission (nm)	560 - 640	460 - 560	830	470 - 520
Life time (S)	1.6×10^{-6}	6.4×10^{-6}	3.0×10^{-9}	1×10^{-9}
Detection limit (mol/L)	2×10^{-11}	4×10^{-12}	10^{-10}	unknown

2.3.4 Compilation and evaluation of thermodynamic data

Two sets of compilation works were planned in this program: the first one is the study of the role of organics in the migration of radionuclides and the second one is the compilation, evaluation and determination of thermodynamic data of hydrolysis and carbonate complexation of actinides.

(I) Role of organics in the migration of radionuclides [Carlsen, 1988]

Carlsen (RISØ) has finished the study on this subject in 1988. The report summarizes the following aspects: The occurrence of organics including natural and man-made organics in the geosphere; the behaviour of organics related with sorption, persistence and microbial degradation process; the complexation behaviour of organics with metal ions, compiling the complexation constants of low and high molecular weight organics, e.g. carboxylic compounds, humic/fulvic acids; the influence of organics on the migration of radionuclides including Tc and I. This is a valuable review work for those who want to gain an overview of the role of natural and man-made organics in the migration of radionuclides in the terrestrial environment. The two important tables from this work are reproduced in Tables 35 and 36, which summarizes complexation constants of carboxylic compounds and humic/fulvic acids of various metal ions, respectively.

(II) Compilation, evaluation and determination of thermodynamic data of hydrolysis and carbonate complexation of actinides [TUM]

The compilation has been finished for the hydrolysis and carbonate complexation of the actinide series from Th to Cm. The verification of individual data has just commenced as for their accuracy and the validity of species assumed in experiment. The report on the compilation will be available in due course.

The new thermodynamic data have been determined for the hydrolysis reactions of Th(IV), Pu(IV), Np(V) and Am(III) and the carbonate complexation of Am(III). A part of them are still at the stage of final evaluation. The solubility products of crystalline PuO₂ and amorphous Pu(OH)₄ have been also determined under well defined conditions after careful speciation of equilibrium solutions. The verified results are:

$$\log K_{sp} (\text{PuO}_2(\text{c})) = - 60.20 \pm 0.17 \quad (\text{I}=0)$$

$$\log K_{sp} (\text{Pu(OH)}_4(\text{am})) = - 57.85 \pm 0.05 \quad (\text{I}=0)$$

which are the lowest values ever determined experimentally [Kim and Kanellakopoulos 1989].

Table 35. Complexation Constants for Selected 1:1 Complexes with low molecular weight organic ligands [Carlsen 1988] (in log scale)

Metal Ion	Acetic Acid	Citric Acid	EDTA	DTPA	NTA
Na ⁺	-	0.7	1.64	-	1.22
Cs ⁺	-0.10	0.32	-	-	-
Ca ²⁺	0.53	3.5	10.61	10.75	6.39
Sr ²⁺	0.43	3.05	8.68	9.68	4.97
Fe ²⁺	1.40	4.4	14.27	16.4	8.33
Fe ³⁺	3.38	11.50	25.0	28.0	15.9
Co ²⁺	1.10	5.0	16.28	19.15	10.38
Ni ²⁺	0.74	5.40	18.52	20.17	11.54
Pb ²⁺	2.15	4.08	17.88	18.66	11.34
Ce ³⁺	1.91	7.39	15.94	20.33	10.70
Eu ³⁺	2.13	7.91	17.32	22.39	11.32
Th ⁴⁺	3.89	-	23.2	28.78	13.3
UO ₂ ²⁺	2.61	7.4	7.40	-	9.50
NpO ₂ ⁺	1.33	3.67	7.33	-	6.80
NpO ₂ ²⁺	2.31	-	-	-	-
Np ⁴⁺	2.68	-	24.6	29.79	17.28
PuO ₂ ⁺	0.83	-	12.90	-	6.91
PuO ₂ ²⁺	2.31	-	16.39	-	-
Pu ³⁺	2.02	18.86	18.12	-	10.6
Pu ⁴⁺	4.89	15.54	25.60	24.00	-
Am ³⁺	1.99	7.74	18.16	22.29	11.5
Cm ³⁺	2.06	7.74	18.45	22.98	11.8

EDTA: Ethylenediamine tetraacetic acid; DTPA: Diethylenetriamine-pentaacetic acid; NTA: Nitrilotriacetic acid

Table 36. Complexation constants and composition of humic/fulvic acid (f) complexes [Carlsen 1988]

Metal ion/ligand	pH	μ	f	log β :
Th ⁴⁺ /HA	3.5	0.1	1.92	6.74
Th ⁴⁺ /HA	3.95	0.1	1.00/2.00	11.1/16.2
Th ⁴⁺ /HA	5.03	0.1	1.00/2.00	13.2/18.4
Th ⁴⁺ /HA	8	0.1	1	17 ^d
Th ⁴⁺ /FA	4.01	0.1	1.00/2.00	9.8/13.5
Th ⁴⁺ /FA	5.00	0.1	1.00/2.00	10.8/15.1
UO ₂ ²⁺ /HA	5	0.1	1.26	5.68
UO ₂ ²⁺ /HA	3.5-7	0.1	1.0	7.8 ^f
UO ₂ ²⁺ /HA	4.04	0.1	1.00/2.00	5.11/8.94
UO ₂ ²⁺ /HA	8	-	1.00/2.00	7.6/11.5 ^d
Pu ⁴⁺ /HA	~ 4	-	1.00/2.00	12.4/17.2
Pu ⁴⁺ /HA	8	-	1.00/2.00	18.8/20.00 ^d
Am ³⁺ /HA	6.5	-	1.00/2.00	6.4/10.6
Am ³⁺ /HA	4.5	0.1	1.00/2.00	7.3/11.0
Am ³⁺ /HA	8	0.1	1.00/2.00	14.4/15.7 ^d
Eu ³⁺ /HA	4.50 ^b	0.10 ^c	1.00/2.00	7.8/10.7
Eu ³⁺ /HA	8	0.10	1.00/2.00	13.3/14.6 ^d
Eu ³⁺ /HA	4.47 ^b	0.05	0.99	6.15
Eu ³⁺ /HA	4.48 ^b	0.05	1.04	6.20
Eu ³⁺ /HA	4.48 ^b	0.10 ^e	0.93	5.88
Eu ³⁺ /HA	9	0.10	1.00	13.9
Eu ³⁺ /FA	4.50 ^b	0.1	1.00/2.00	6.9/11.0
Eu ³⁺ /FA	3.2	0.3 ^e	1.00	6.9

a): each line in the Table corresponds to a single fulvic acid type; b): acetate buffer; c): μ adjusted by KCl; d): estimated by extrapolation from experimental data; e): adjusted by NaCl; f): no pH variation is given;

This research program is expected to produce a MIRAGE data base for the hydrolysis and carbonate complexation of actinides, which may support the CHEMVAL program and can be used as a reference for individual migration studies. Direct and indirect supports from the MIRAGE members are welcome.

2.3.5 Theoretical prediction of sorption phenomena

This subject is conceived to promote theoretical predictions of sorption phenomena of radionuclides in a given aquifer systems. The work carried out in this aspect is a review made at BGS [Falck, 1989] for modeling the interaction between natural organic matter and metal ions. The content of this review work is summarized below.

The report reviews techniques available to model the interaction between natural organic matter (mainly fulvic and humic acids) and protons and metal cations. Approaches to model the interaction between cation and organic macromolecules can be divided into two groups: "discrete ligand models" and "continuous distributions models".

Discrete ligand models assume a known concentration of known ligands with known properties (like stability constants) and model the distribution of cations/protons between those and possibly inorganic ligands in very much the same way as do the well known speciation codes. Thus they are readily compatible with the latter. They only take into account true binding, unspecific electrostatic interaction being neglected. Conformational changes due to changes in the environment are also neglected.

Continuous distribution models are mainly employed to analyse experimental (titration) data and are distinguished by the transformation of the data set the analysis is performed on (raw titration curves, cumulative curves etc.). The aim is to describe the often complex shape of these curves with as few parameters as possible. In the case of the statistical distribution models this is done by fitting well known statistical distributions (e.g. a Gaussian, which has three adjustable parameters) to the experimental data. Since there is no a priori assumption about the number and character of binding sites these models easily accommo-

date non-specific secondary interactions. However, their predictive capacity is limited to interpolations within the range of experimental conditions and they are incompatible with current speciation models.

At present there is no comprehensive model available which includes all the phenomena over the whole range of environmental conditions of interest which have been observed for natural organic matter and which will determine significantly their binding behaviour.

3. CONCLUSIONS AND PROSPECTS

Complexation of radionuclides with natural organics, e.g. humic acid, and colloid generation in natural aquifer-systems are two new subjects that are attracting more and more attention in the safety assessment of nuclear waste repository in the geosphere.

The long-lived actinides and some fission products of higher oxidation states ($Z \geq 3+$) have generally a strong tendency to complex with natural organics or to form colloids, either real- or pseudocolloids in natural aquifer systems. Through such geochemical processes the instability of the metal ions of higher charge in neutral aqueous media would become compensated and hence they could be stabilized in a given groundwater. Resulting effects on the migration of the radionuclides will be considerable.

Although the geochemistry of humic substances as well as colloids have become a more or less well established research field, the knowledge in this field is not yet sufficient to provide satisfactory answer to the problems associated with humic substances and colloids in the migration chemistry of radionuclides. Much more fundamental knowledge on this subject is required, than now available in the present state of migration chemistry, in order to delineate the effects of organic substances on the migration phenomena of individual radionuclides in the form of quantified parameters. Such quantification will certainly help and is essential for the proper modeling of the safety assessment. Because of its cardinal importance, research area No. 1 of the project MIRAGE II has been confined to the acquisition of basic knowledge on humate complexation and colloid generation in natural aquifer systems.

Furthermore, the application of this above mentioned basic knowledge is envisaged to promote an understanding of radionuclide retention phenomena in various site specific aquifer systems under the influence of natural organics and colloid generation.

The whole work is still in progress partly in a coordinated process such as the interlaboratory comparison exercises, and partly in individual research directions to deal with particular site specific problems. The results of every research theme will be directly or indirectly beneficial to all participating laboratories.

It is too early to draw conclusions on any of the research that is still in progress. However, some comments can be made concerning the on-going work and also the prospects for new contract research themes started 1988.

3.1 Interlaboratory comparison exercise

a) Characterization of humic acids

- This exercise demonstrates the analytical capacity of individual laboratories together with the confidence rating of their analytical results
- The best results of characterization have been attained for the reference humic acid: HA(H⁺)-Aldrich and the first site-specific humic acid: HA(H⁺)-Gohy 573.
- Crucial difficulties involved in experimental handling of humic acids are recognized, especially in the determination of proton capacity and molecular size distribution; necessity of simple straightforward new methods for the determination of proton capacity and molecular size distribution is recognized.
- Continuation of the interlaboratory comparison exercise appears beneficial for the improvement of individual laboratory capabilities and the acquisition of well proven data from characterization; so is the practice being continued for the second site-specific humic acid: HA(H⁺)-Fanay-Augères.

b) Complexation of radionuclides with humic acids

- Different procedures envisaged by various laboratories for the complexation study will provide a chance to recognize evidence of shortcomings of individual methods and hence to establish a well proven procedure for the purpose
- The exercise will give a good chance to verify the available literature data and produce reliable data with sound foundations.
- Chemical complexation processes of metal ions with polyelectrolyte ligands are still not well understood, so that interpretation of experimental results is often relied on a mathematical fitting rather than on the verified probable chemical conformation. Thus resulting interpretation of 1:1 and 1:2 complexes of metal ions ($Z \geq 3+$) with humic/fulvic acid is difficult to understand.
- Any polyelectrolyte, like most ion exchangers, has a loading capacity for a given metal ion in solution, which varies accordingly with pH and ionic strength. The thermodynamic complexation constants of metal ions with humic/fulvic acid must be evaluated in accordance with the loading capacity. This process would provide the data independent of pH and ionic strength, like other thermodynamic data, e.g. hydrolysis, carbonate complexation etc. such data are then comparable with one another.

c) Colloid generation

- Comparison exercise of the sampling will provide a sound basis for the selection of an appropriate method for the study of natural aquatic colloids in general
- Size distribution study by SEM micrograph technique is useful but limited to colloids of non-aggregation. Major shortcomings of this technique are its incapability of counting smaller colloids (< 50 nm) and the aggregation occurring during the sample preparation.

- Photon correlation spectroscopy has not yet been proven to be an appropriate method to enumerate the colloid population and size distribution in groundwater
- Laser-induced photoacoustic spectroscopy (LPAS) is useful for the direct estimation of total colloid population in groundwater but its capability is yet to be verified carefully.
- Development of a suitable new method is necessary for the determination of the colloid population and size distribution.

3.2 Colloid generation

Apart from the colloid characterization that gives primary qualities to understand, the generation mechanisms of colloids in different kinds in natural aquatic systems are also of great importance to the migration of radionuclides. The generation of real-colloids and pseudocolloids involves a variety of complicated processes which are not yet well understood. The colloid generation mechanisms have been in general not investigated separately but as an integral study of the near field chemistry, e.g. leaching of solidified wastes, or the migration process in batch or column experiments. The generation of real-colloids and pseudo-colloids of transuranic ions, and the transition of humate complexes to humic colloids are being investigated intensively. Further study is still necessary for this particular subject.

3.3 Basic retention mechanisms

The ultimate objective of the basic geochemical study of actinides and fission products is to understand retention mechanisms of individual radionuclides in a given aquifer system and thereupon to validate retardation parameters to be used for modeling. Because of various approaches to an understanding of retention mechanisms, there are numerous research proposals related to this subject which have commenced 1988. Knowledge on a variety of new aspects in the basic retention mechanism are already available from these research projects, as summarized below:

a) Influence of natural organics and colloid generation

- Presence of humic acid increases the Am solubility in cementitious solutions; competition in the complexation of humic acid with the Ca^{2+} ion in the system is obvious.
- TcO_4^- undergoes reduction in its interaction with humic acid and hence possibly migrates with humic acid. The TcO_4^- ion is also reduced readily on the surface of pyrite (FeS_2) to form TcS_2 , which becomes evidently immobile in clay formations. The geochemical interactions of TcS_2 with humic acid is still to be investigated.
- Influence of natural organics, e.g. humic acid, citrate and man-made organics, e.g. EDTA, on the diffusion of NpO_2^+ in different uncomplexed clays (Montmorillonite and Kaolinite) are not observed. In the clays complexed with humic acid, a change is observed in the diffusion NpO_2^+ . However, more study is necessary for a better understanding of underlying processes.
- Experiment of colloid retention demonstrates that pure ceria colloids (CeO_2) are sorbed on mica and silica surfaces whereas colloids of ceria coated silica do not show adsorption on these mineral surfaces.

b) General retention mechanisms in sorption experiments

- Results available in this subject are only preliminary and, therefore, no useful conclusion or comment can be made at the moment.

c) Speciation of radionuclides in geochemical processes:

- Direct speciation of actinides in natural aquifer systems provide explanations of chemical processes involved in the solubility and sorption behaviour.
- Such a speciation facilitates the validation of geochemical modeling which remains otherwise unsubstantiated theoretical predictions.

- High sensitivity speciation becomes possible by modern laser Spectroscopies using different detection Techniques: photoacoustic, thermal lensing and time resolved fluorescence measurements.

d) Compilation and evaluation of thermodynamic data:

- Critical review on the role of organics in the migration of radionuclides is available; proper interpretation for the application of humate/fulvate complexation constants known in the literature to geochemical modeling is yet necessary.
- Much of thermodynamic constants for the hydrolysis and carbonate complexation of actinides are found to be sheer numbers which require still verification by speciation and thermodynamical correlation.

e) Theoretical prediction of sorption phenomena:

- Sorption phenomena of radionuclides can be theoretically predicted, provided all necessary geochemical data bases are available and reaction mechanisms are known. This is a long range task which can only be solved by multi-laboratory cooperation.

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Review of work done in Research Area

"Calculation tools"

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1. INTRODUCTION

The research and development effort in the area "calculation tools" of the MIRAGE project consists of ten contracts in five different countries. At the time of last year's review, several of these contracts had just begun and little progress had yet been made. This year, significant advances have been made in all cases, although in most instances the work is not yet completed and final reports are only due in 1989 or 1990. In many areas it is therefore difficult to draw any final conclusions.

If the mood of the modelling community were to be described in a few words, it seems that, with rare exceptions, "doubts" and "disillusion" would today be the appropriate terms. This should not be taken negatively : rather, it is a healthy sign of "maturity" to realize that life is not simple, and that the application of models to more and more complex situations brings more and more difficulties which the modelling teams had perhaps not anticipated. It also shows that there is room for improvement, and that more and more models are applied to the real world and not confined to generic, self-defined problems.

Now, if a trend were to be defined in the effort of the modelling community, it would probably be appropriate to highlight the words "quality assurance-quality control" which seem to be of common concern. It is probably a very important trend, especially for modellers but also for any research programme, and we will discuss it in some detail.

To organize the present discussion, we will use the following classification of the modelling effort : (i) Model application ; (ii) Model improvement.

2. WORK REVIEW

2.1. Model application

2.1.1. Interpretation of in situ tracer tests at DRIGG, UK

This is a joint effort of the British Geological Survey (BGS), UK

and the Delft Geotechnics (DG), NL. Let us recall (see last year's MIRAGE review) that the aim of the experiment is, for the BGS, to understand and compare tracer tests in a thin "homogeneous" sandy aquifer at a meter scale, with conservative and non conservative tracers, and for the DG, to attempt to validate a modelling concept for "natural" porous media, where the role of the clay lenses and small scale heterogeneities of the medium can be accounted for by a continuous layering of the system, even if the "real" system is not layered (contract n° 64 and 83).

Two tracer tests were carried out by the BGS in 1988, involving conservative tracers (chloride, iodide, tritium). Measurements of tracer concentration as a function of time were obtained in 6 multilevel samplers 15 m apart, for 3 piezometers at distances ranging from 0.60 to 1.60 m from the tracer injection well. The porosity of the formation was estimated at 0.35 from core measurements, and the permeability was measured at different elevations in two piezometers less than a meter away from the tracer path. These measurements were obtained by means slug tests performed with special equipment forced into the ground and successively opened at different elevations 0.2 m apart (see research area "in situ migration experiment").

Although the 1.5 m thick sand layer appears at first sight "homogeneous", both the permeability measurements and the breakthrough curves of the tracer at the 6 different elevations in the piezometer show an important heterogeneity or layering.

The BGS used an analytical model to interpret the experiments : the flow field is shown to be almost parallel between the tracer injection piezometer and the sampling piezometers ; therefore, a one-dimensional solution (neglecting transverse diffusion) was used. The interpretation was made assuming perfect independent layering at each of the 6 sampling elevations, and gave very small longitudinal dispersivities (0.5 to 3.6 cm) i.e. 1/100 of the tracer displacement length as is usually the case when multilevel samplers are used. The disturbing finding is, however, that with the tracer breakthrough times, it is also possible to estimate the vertical distribution of the permeabilities. These are shown in figure 1, together with those determined from the slug tests : they match neither on the average, nor in the possible trend, if there is one. We will discuss later the implications or possible explanations.

The DG used a numerical code, VERA, initially developed by INTERA, but later improved by DG, and also assumed parallel flow, thus representing the system in a two-dimensional cross-section. This is equivalent to the BGS hypothesis, except that it allows vertical transverse dispersion between the layers. The DG claim was that "heterogeneous" systems could be modelled by layering ; they therefore introduced 6 different layers in their model, the permeabilities of which were extrapolated from the 2 series of slug test permeability measurements carried out by the BGS. The numerical model was, of course, first verified and compared with analytical solutions. Breakthrough times predicted with this model compare very poorly with the observed ones, as shown e.g. in figure 2, for one of the layers, with a discrepancy factor of up to 4. This comes as no surprise, given that the BGS also found very poor correlation between the measured permeabilities and the ones inferred from the interpretation of the breakthrough curves.

What are the implications of this work at this stage ? The quality of the teams, the models, the experiments are out of question : they are among the best available ; the net results are simply that trying to predict conservative tracer transport at a very detailed scale of about 1 m, in a reputedly homogeneous formation, using permeability measurements made at the same detailed scale, produces discrepancies in travel time of up to a factor 4. It can be said that :

(i) the permeability measurements were not representative, since they were not taken exactly along the flow path (approximately 2 m away). The question is then : how many permeability measurements will we need in a "heterogeneous" formation in order to predict transport from a repository ?

(ii) The method of permeability measurements (slug in a short, open section of a borehole) is not adequate. There is no obvious reason why this should not be a valid method ; it has been used regularly and successfully in the past, only the equipment used by the BGS is new and apparently efficient. The DG would like, when the planned experiments are over, to have new series of permeability measurements made to try to resolve this issue.

(iii) Is a discrepancy of 4 between predictions and reality really all that bad ? When a model is used to predict groundwater travel time from a repository to the accessible environment, what uncertainty will be consi-

dered acceptable ? Should we not begin to realize that predicting the behaviour of the geosphere may always involve a large uncertainty and, if feasible, build repositories with this in mind ?

It can also be said that the discrepancy of 4 was obtained when trying to predict the detailed behaviour of each single layer, which may not be required in an assessment. If we compare the discrepancies between each layer and predictions made by the BGS for a homogeneous equivalent layer for the breakthrough times, we find "only" a discrepancy of 3 for the 1st observation well, and of 2 for the 3rd well ; as can be expected, the role of heterogeneities may average out over larger distances.

(iv) More fundamentally, this experiment emphasizes a theoretical difficulty which has been reported several times (see e.g. MARSILY, 1988, DIEULIN, 1980). Point measurements of permeabilities (or velocities) are Eulerian measurements, whereas tracer tests give access to Lagrangian measurements (Eulerian is equivalent to "at fixed location in space", Lagrangian to "along a trajectory"). It is clear that the two are not equivalent and that trying to predict one from the other is similar to violating the 1st or 2nd principle of thermodynamics, for heterogeneous media. In simpler terms, if there is in the system a few localized short circuits, the water will find them and flow through them, whereas local measurements will, in general, miss them. The real question is whether we can, on other grounds, predict the existence of these short circuits and model them. If not, one must realize that some regulations concerning nuclear waste disposal, which require a minimum groundwater travel time between the repository and the accessible environment (e.g. 1,000 y in 10 CFR 60 of the US National Regulatory Commission) cannot be complied with through the available measurement methods.

How will this work be continued ? First of all, the BGS will conduct additional tracer experiments using mildly sorbed elements, probably Cobalt or Nickel complexes with EDTA or natural organics (see research area "Geochemistry of actinides and fission products"). Preliminary laboratory experiments are under way to test these complexes with the soil, in batch experiments and column experiments (advective or diffusive) in order to estimate K_d 's or retardation factors. The stability of these complexes is also estimated using geochemical speciation codes such as PHREEQE with the Harwell Data Base. Then the comparison of the predicted retardation factors with those determined in the field, where the conservative and non conser-

vative tracers are compared, will indicate what additional uncertainty must be included when predicting non-conservative transport. Modelling will be used to interpret these tests. It may also be possible to obtain average concentrations in the aquifer together with the detailed multi-level information, in order to determine the possible reduction in uncertainty when averaging is done. Finally, when the experiments are over, additional permeability measurements may be made on the exact location of the direct flow line between the injection and observation wells, which can then be compared with those deduced from the tracer test. The final aim should be to be able to estimate the uncertainty attached to predictions of the transport of conservative or non-conservative elements, from various levels of reconnaissance of the medium properties.

2.1.2. Geochemical modelling in France

The CEA and the Paris School of Mines have previously developed a coupled geochemical transport code, STELE, see e.g. the 1988 MIRAGE review, or COUDRAIN-RIBSTEIN, 1988 (contract 75). In order to try to validate this code, column experiments were performed at the CEA-Cadarache. The material used is a crushed limestone, calibrated between 0.250 and 0.315 mm, containing 6 to 7 % of clay. The major flow through experiments carried out on the columns consisted in injecting SrCl_2 at different concentrations and temperatures and observing the break-through curves as a function of time. The modelling represented transport with the phenomenon of precipitation/dissolution of calcite and strontianite, and included the temperature dependence of the thermodynamic constants, the variation of temperature with time and a first-order kinetic representation of both calcite and strontianite formation/dissolution. The thermodynamic data base used for the calculations was the one assembled in the CEC CHEMVAL exercise. Although the geochemical system was selected for its simplicity, the experiments were extremely difficult for the modellers to interpret, and the results rather disappointing (VINSOT and COUDRAIN-RIBSTEIN, 1988) : unexplained phenomena were observed, the measurements were sometimes questioned, the first-order kinetic model was found to be inadequate, and the role of sorption on the clay, which was not represented, was found to be very significant, although difficult to predict on only thermodynamical grounds. Figure 3 shows an example of observed and calculated breakthrough curves for Sr and Cl in the column, which, although difficult to compare, indicate that the major variations are

reproduced only very reproduced.

Clearly, both the experiments and their interpretation need to be improved ; but again, the question arises of the degree of accuracy with which models are supposed to predict the future. Are we following the right track in developing more and more sophisticated models, when we realize that it is very difficult to validate them and to independently determine the parameters that they need ? Our implicit assumption is that the better we understand and represent the physics of the system, the more reliable our predictions. I still believe that this is the correct approach, although the present results do not support this belief.

2.1.3. Thermo-hydro-mechanical modelling in France

The CEA (ANDRA and DEMA) in France is using models to try to predict, in crystalline rocks, the impact on the hydraulic behaviour of the system of the thermal loading of the repository by HLW (contract 148). The modelling will be fully coupled, including (i) the transient thermal evolution of the medium by conduction ; (ii) the ensuing thermal stress changes and the resulting changes in the fracturing and the hydraulic fracture properties of the medium ; (iii) the influence of the heat on the fluid flow (buoyancy forces), taking into account the changes in the fracture density and properties.

This very ambitious scheme, not yet completed, is being applied in two dimensions in a cross-section representing the Neuvy-Bouin granite (Deux-Sèvres), which is one of the four potential sites at present under investigation in France for HLW disposal. However, the site properties (except topography) are generic, since no information is, as yet, available at depth.

The cross-section represents a 4500 m (length) by 1500 m (thickness) section of the formation, the repository being represented by a continuous zone of 1500 x 60 m at an average depth of 500 m. The finite element method is used, assuming continuous equivalent medium properties. The temperature changes have been calculated up to 10,000 years, with a peak temperature at the repository of 90°C, i.e. corresponding to 30 year old reprocessed waste and a relatively moderate density. The mechanical stresses have

been calculated over the same time period ; the model assumes a "no tension" behaviour but with some strain-softening, for coherence and numerical stability. The assumed mechanical rock properties are in the ordinary range ($R_T = 10$ MPa, tensile strength, $E = 74,000$ MPa, Young's modulus, $\nu = 0.26$, Poisson's ratio). Fissures are then assumed to occur in the directions orthogonal to the principal direction of the tensile stress, if it exceeds R_T . Figure 4 gives an example of the locations of the fractures in the system, after 100 years. The initial stress field prior to heating assumed no residual regional stress, and the boundary conditions were either zero displacement or prescribed stresses. The positions of these boundaries were chosen so as to limit the size of the problem, and may still be too close to the repository not to influence the results, but this can be improved in the future. The main difficulty is now to determine the changes in the permeability of the equivalent medium in the areas where fracturing occurs. The mechanical calculations provide an estimate of the direction of fracturing and of the porosity increase per element but are unable to determine whether one or several fractures will open (or reopen : so far, no pre-existing fractures are considered ; similarly, fractures are assumed to be able to close again perfectly when the thermal stresses are relieved). The plans are to assume that one single fissure will form, to determine its directional permeability using the "cubic law" based on its calculated aperture and to add this permeability increase to the permeability tensor of the considered element of the mesh. This work (or work on other assumptions) remains to be done, and its validity will have to be assessed.

Preliminary hydraulic calculations have, however, been made. The forces driving the flow are both the pressure gradient prescribed by the elevation of the ground surface and the buoyancy forces due to the thermal loading in the so-called Boussinesq approximation. The domain used for the flow calculations is larger (8075 x 1500 m) in order to limit the influence of the arbitrary no-flow lateral boundary conditions. The upper surface has been prescribed as a constant flux boundary condition, but will later be prescribed as a constant head, which seems more realistic for a low permeability medium in a temperate climate. Path-lines have been calculated for particles released at the repository at initial times between 0 and 5,000 years, and for travel times of 5,000 years after their release, see e.g. figure 5.

These hydraulic calculations, which do not yet take account of the permeability changes as functions of time due to the thermal stresses, will be used as references of comparison with the cases where these changes will be included. Given the porosity increase calculated with the thermo-mechanical model (up to $3 \cdot 10^{-3}$ which is, a very large figure, equivalent to a fracture of 3 mm every m) it is expected that the coupled effect will be very large. Several hours of computer time on a CRAY machine are required for these very complex coupled calculations.

The question then arises : will we ever be able to validate such a complex model and determine whether the many simplifying assumptions, that are needed to make the model tractable, are valid (2-dimensionality, equivalent continuous properties, no-tension behaviour, fracturing and permeability changes...) ? How will we measure the required parameters in the field ? What kind of experiments are needed both for validation and parameter determination ? The Fanay-Augères thermo-hydro-mechanical (THM) experiment performed by the CEA will be used as a first attempt at validation, but is its scale (a $10 \times 10 \times 5 \text{ m}^3$ block of fractured granite) sufficient to be representative ?

Finally, if the uncertainty associated with the exact consequences of the thermal loading of a fractured system is large and cannot be easily reduced, should we keep such an option open for HLW disposal ? Probably yes, because effects of this kind can be controlled by adequate repository design, CEC, 1982). Modelling at this stage is a tool for sensitivity analysis, responding to questions of the "what if" type but is this enough for licensing a repository ? To answer these questions, a full performance assessment of the repository behaviour may be required, coupled with complex thermo-hydro-mechanical calculations.

2.1.4. Flow and transport calculations in the Netherlands

At the RIVM, in the Netherlands, the finite element flow and transport code METROPOL, developed within the framework of MIRAGE, has been applied to a large variety of problems (contract 81).

(i) The principal one is a generic safety assessment performed for the Dutch Government to evaluate the acceptability of salt domes as a host

medium for HLW. The regional geology in the Netherlands has been represented on a 2-D cross-section ; however, all the parameters are generic, since no site-specific information is available. The METROPOL code is used in conjunction with two other models : the source term model EMOS, developed by the GSF in the FRG and run at the ECN, representing an accidental situation, where brines and radionuclides are expelled from the repository through a fracture or backfilled galleries after accidental water intrusion ; the dose model is the BIOS code, developed by the NRPB in the UK (this shows, by the way, that cooperation and exchanges between modellers in the EC do exist !). A very large number of scenarios have been analysed with the flow model, considering the occurrence within the next 10^5 years of several external geodynamic processes such as glaciation, erosion and filling up of valleys, sea level changes, etc, which are certain to appear within this time frame. For each scenario, calculations have been made of travel time from the repository to the environment, and from these, 7 cases have been selected for radionuclide transport calculations. These are done in 1-D along a flow path, considering up to 46 different nuclides ; chain decay and instantaneous linear reversible sorption are included, the K_d values are taken from the NEA data bank, the GORLEBEN site, and from RIVM data for superficial alluvial deposits. Several options were considered, e.g. a shallow salt dome or deep bedded salt, and disposal by deep boreholes or by conventional shaft and mining operations. The report will be released by the Dutch Government in the first semester of 1989 and provides comparisons between the various options and scenarios, which will be of high interest to all the EC Countries. In terms of modelling, the study also pointed out the need for further optimizing of the code, given the very large number of calculations that are required. Although METROPOL is already vectorized for the CRAY machine, which uses a single processor, the need is felt to parallelize the code for running on an ALLIANT FX40 machine which uses 4 processors in parallel. Large savings of CPU time are expected by using preconditioning and conjugate gradient techniques for solving the linear equations. More elements are also considered necessary to improve the precision. Finally, performing transport calculations in 1-D is considered acceptable, provided that the flow path has been calculated correctly in 2 or even 3-D, taking into account the brine density effects, which are vital for the salt option (see below).

(ii) Several attempts at validating the METROPOL code have also been made, essentially within the HYDROCOIN and INTRAVAL projects, or within

PAGIS in cooperation with the GSF. The emphasis has been on the testing of flow problems with dense brines, which is one of the most difficult and less "certain" areas of flow modelling, since no analytical solutions exist with which to compare the numerical calculations, and furthermore, the very theory behind the models is questioned (see below, iii). Within PAGIS, the GORLEBEN site has been modelled in 3-D, and compared with results obtained by the GSF using the code SWIFT. A regional and a local model were set up, with transfer of the boundary conditions from one to the other. Although good agreement was obtained when only freshwater flow was represented, it was found that when brine flow was considered, the mesh size became inappropriate, and very strange velocity fields appeared, which were probably numerical artefacts, although this is difficult to ascertain, as density differences may indeed create local convective cells. Tests using finer meshes, or yet mixed elements (finite elements which conserve mass over each mesh) may be of interest. It is worth mentioning here that the same difficulties appeared in France with the code METIS, in attempts to simulate flow in the deep aquifer of the Dogger in the Paris basin, where dense brines leaking upwards from the Triassic sandstones mix with freshwater : very strange, mesh-dependent velocity fields were calculated, that could not be validated. In the GORLEBEN case, some of the difficulties may also arise from the very large permeability contrast (up to 10^7) within the various layers and from the anisotropy ratio (10). The provisional conclusions drawn from this test are that standards of comparison would be highly desirable, and that mesh-dependence of the solution should be eliminated by refining the mesh until a stable solution is found, which might tremendously increase the size of the problem.

With SWIFT, density dependent problems are for this reason found to be too expensive to run. It is worth noting that a steady state problem can only be calculated as the result of a very long transient calculation ; for instance, in the case of GORLEBEN a period of 3,000 years was needed to obtain equilibrium (Figure 6). This makes the calculations even more costly.

Within HYDROCOIN, the Level 2 Case 2 known as the ELDER experiment was calculated. This is a thermal experiment performed in Cambridge in 1967. The test was run using the so-called Boussinesq and its first extension approximations (mass per unit volume variable in all terms of the equation, not only in the velocity term, but with constant viscosity), and using

different mesh sizes. It was found again that very fine meshes were required, but the main finding was that thermal experiments are inadequate to validate the dense brine flow problem, since the mass per unit volume changes created by temperature variations are much too small to represent brine density changes : in the first instance, the classical Boussinesq approximation is valid, whereas in the second it is not.

The HYDROCOIN Level 1 Cases 1 and 2 (flow towards a well, flow in a fractured medium) and Level 2 Case 4 (flow in the Piceance Basin) were also run successfully, which again underlined the need for finer meshes, and for improving the finite element method in order to locally conserve mass.

In the Piceance case, which included a fitting of the model, the validation of the model was found hard to make convincing.

(iii) As was reported in the 1988 MIRAGE review, the RIVM is also conducting a brine flow experiment in the laboratory. This experiment is not only meant to serve as a basis for validating METROPOL, but also to test whether the theory of brine transport needs to include two new additional terms (one in the formulation of Darcy's law, one in the formulation of Fick's law), which are generally neglected, but ought to be present according to thermodynamic principles (HASSANIZADEH, 1988 ; HASSANIZADEH and LEIJNSE, 1988, see also 1988 MIRAGE review). These new terms act with an "efficiency factor" which needs to be experimentally determined. Both freshwater flow and dense brine flow experiments have been performed but are still inconclusive at this stage. A small deviation is indeed observed between the two experiments and has been modelled with METROPOL, indicating, at least, that the new theory may be better than the old one ; however, the changes are too small to be unquestionable, given the precision of the measurements and experimental artefacts, e.g. apparent clogging of the medium. Additional work is still required on this important issue.

(iv) In parallel with the above model applications, several improvements of METROPOL have also been accomplished this year, such as post-processing of the results, plotting particle trajectories, vectorization, etc. and publication of a User's Guide. Discussions with the BGR in the FRG are also under way to make METROPOL available to them ; the use of the code in the Netherlands for environmental problems is also under consideration.

In the future, temperature effects in the transport part of METROPOL need to be incorporated, as planned in the contract, as well as matrix diffusion, colloids, geochemical modelling, adaptative grid refinements, probabilistic modelling, mixed elements, and, above all, validation and confrontation with experimental work. There is still a lot to do before predictive calculations of radionuclide transport inside a dense brine flow system can be accepted as valid within a well-defined uncertainty range, for a real site...

2.1.5. Modelling at MOL, Belgium

The GEN-SCK in MOL is pursuing parallel studies in regional modelling of the flow through the Boom Clay and adjacent aquifers, and modelling of laboratory or in situ experiments of radionuclide migration in clay plugs, under advection or diffusion (contract 55). Both areas are closely connected with real measurements. Regarding the regional modelling, a first multilayered finite difference model NEWSAM was fitted during the mid 80's on the geohydrologic data, and used to estimate a leakage flux through the Boom clay. At present, the geochemical data collected on the system (adjacent aquifers and clay pore water) are being studied in an attempt to further validate this flow model. In particular, additional ^{14}C measurements within the clay pore water have been made, which do not seem to confirm the 1984-85 values (giving an age of around 30.000 years inside the clay). This is somewhat reassuring, since these "young" ages of the clay porewater could only be explained in the flow model, given the estimated leakage flux through the clay, by using a clay porosity accessible to inorganic carbon of a few percent, which is not on the order of the laboratory measurements, which are in the 30 % range. The GEN-SCK is now looking into the use of ^{36}Cl data (half-life 308.000 years) to ascertain the age of the clay pore water and thus possibly validate the leakage flux estimated with the NEWSAM model. It also envisages a possible future use of a finite element model (maybe the RIVM METROPOL model, or the French METIS model) to represent the regional flow in order to compare the advantages and disadvantages of these two modelling techniques on the same site.

On the modelling of radionuclide transport in clay, the emphasis is at present on the definition of the "accessible porosity" of the clay, which is both radionuclide and consolidation pressure-dependent. PUT and

HENRION (1988), PUT et al. (1989) have shown how to interpret the diffusion and the flow-through experiments on clay plugs, and to determine the apparent diffusion coefficient for each element or radionuclide. The code used for these interpretations is a version of the MICOFF code, already presented in several earlier MIRAGE reviews. Many previous authors have interpreted similar tests with sorbing nuclides by introducing a new concept, that of "surface diffusion" of the sorbed elements on the clay surfaces, e.g. RASMUSON and NERETNIEKS (1983), MURINEN et al., 1985, 1987. PUT (to appear, 1989) was able to show, using the same experimental data as the previous authors as well as new measurements at MOL, that one is justified in interpreting the data without any surface diffusion, by simply allowing the accessible porosity of the sample to be nuclide dependent. This assumption is coherent with the expected attraction/repulsion effects of charged nuclides with negatively charged solids and with molecular size effects (thieving) of macromolecules. Such effects are clearly shown when the total porosity of the samples is decreased, e.g. by increasing the consolidation pressure (figure 7). Changing the ionic strength of the solution also changes the anionic repulsion effect, and thus the accessible porosity.

When diffusion experiments are performed by contacting labelled and unlabelled clay plugs, several additional phenomena have to be accounted for in the modelling, such as : differences in accessible porosities of the samples, suction of the solution from one sample to the other, if they are not exactly at the same capillary pressure, influence of the end filter plates on the plugs, etc. All these effects have been accounted for in the model. However, only the diffusion coefficient can be determined from these experiments, not the accessible porosity (Figure 8).

Finally, the same MICOFF model is used to interpret the in situ migration experiments where advection of the natural formation pore water is imposed on labelled clay plugs introduced in situ at the end of boreholes drilled from the experimental drift. Europium and ⁸⁵Sr data have been interpreted, giving coherent results for the retardation factor based on both the concentration breakthrough curves at the outlet of the plug and the bulk concentration inside the plug, obtained by slicing it at the end of the experiment (see research area "in situ migration experiments").

For these very small-scale experiments, measurements and models

seem to validate and complement each other, making at least one modeller happy in the MIRAGE programme !

Let us also finally mention the planned macro-permeability test in the Boom clay to be performed from the experimental drift by drilling a 5 m long screened hole in the clay and monitoring the incoming flowrate and the pressure field in situ around the borehole, with the aim of calculating the permeability. Design calculations of this test have been carried out in France for the CEN-SCK, using the METIS code (CEN-SCK, 1987).

2.2. Model development

2.2.1. Geochemical modelling at RISØ, DK

The WHATIF geochemical code series is constantly being improved (SKYTTE JENSEN and JENSEN, 1988, 1989, contract 79). WHATIF-AQ (equivalent to EQ3) calculates the speciation of a solution in thermodynamic equilibrium for the major elements. These are at present defined as the more usual ions, i.e. Na, K, Mg, Ca, Sr, Al, Si, Fe, F, Cl, S and others, but any new major elements (e.g. U, Am, Pu) can be introduced. Major elements are also now defined as having a total concentration larger than 10^{-8} molar ; otherwise, they are classified as traces. The programme can handle multi-element ion-exchange directly as well as equilibria with solid phases. The major advantage of this distinction between "majors" and "traces" is that only the majors, that contribute significantly to the overall mass balance, are initially taken into account, thus prescribing the conditions to which the trace elements have to adjust. Both the dimensionality and the computing time of the problem are thus reduced.

WHATIF-AQ has been rewritten in TURBO-PASCAL instead of the earlier BASIC version. The efficiency in computer time was increased by a factor of around 50 ! It can calculate either the solution in equilibrium with an unknown amount of solid phases (their number is specified by the phase rule), or the amount precipitated to reach equilibrium from a supersaturated solution.

The WHATIF-PW code (equivalent to EQ6) can provide the path followed by a solution reaching step by step equilibrium. It is yet to be trans-

lated into TURBO-PASCAL to increase its efficiency. It can handle coprecipitation and solid solutions.

In both programmes, ionic strength is calculated with DAVIES' equations, and the unknowns are expressed as log C, to force a positive solution. Ion exchange is operational for strongly acid exchangers, e.g. clay ; surface of oxides, weakly acid exchangers or surface complexation phenomena need to be included. If the ion exchange capacity of the minerals is known for a given geochemical solution, the equivalent K_d of a given element in the solution can be predicted.

Solid solutions are included in the model for ideal solutions, for trace element behaviour. The ratio of the trace elements coprecipitating with the major element, assumed much smaller than 1, can be predicted from the mineral stability constants. Supporting laboratory experiments with coprecipitation of Europium with calcite have validated the model, and incidentally shown that calcite can act as a good barrier to nuclide migration !

Stochastic modelling representing aquifer spatial variability is also under preliminary investigation at RISØ. They are looking at the effect of attributing random values to the diffusion coefficient in a numerical diffusion model (figure 9), but this still needs to be coupled with geochemical reactions.

Work on geochemical data bases is also progressing at RISØ, in cooperation with CHEMVAL (contract 80). The emphasis is on assembling data concerning the kinetics of reactions. It is well-known that some chemical elements, that should be produced according to the thermodynamic equilibrium theory are, in practice, never observed, because the rate of the reaction is too slow. Rather than an attempt at determining (accurately) these reaction rates, the chosen approach is to investigate whether, in a given set of conditions, most important of which is temperature, a given mineral, is "likely" to form. This "likelihood" could be based on the occurrence of such minerals in nature. Then, "unlikely" minerals could be eliminated from the equilibrium reactions. A programme to manage thermo-chemical data, PMATCH, has also been developed, in cooperation with Dr. F.J. PEARSON, Jr. and J.D. AVIS from Intera Technologies. This programme can be used to render available data that are internally consistent i.e. to refer to the same set of funda-

mental standard data, and to review and compare the most widely used data bases. This work will also be reviewed in section 2.3 on the CHEMVAL study.

2.2.2. Geochemical modelling work at the BGS, UK

Apart from the work already described in section 2.1.1. on the modelling of the tracer experiment at Drigg, UK, geochemical modelling is also under way at the BGS. The PHREEQE code was used to determine the speciation of the groundwater using the Harwell data base and estimate the possible complexation of cations with fulvic and humic acids, especially Co, Ni, Cs and Sr which can be used as non-conservative tracers. It was found that calcite is below saturation, thus precluding the co-precipitation of Cs and Sr, but that $\text{Fe}(\text{OH})_3^0 - \text{Fe}^{++}$ is the dominant redox sensitive system. CO_3^{2+} would then be the dominant species and strongly sorbed by the sediments. Ni could easily form neutral carbonate complexes. It was thus decided that a level of at least 3 mg/l of EDTA should be added to the injected tracer solution, to complex the planned 2 mCi of ^{60}Co which can be used as tracer. Tests of these tracers in batch, diffusion and column experiments are under way. The formation of complexes and colloids is evidenced with various complexing agents, and their stability constants and kinetics of dissociation are determined (see the review of research area "in-situ experiments").

Model development is taking place at a very different level : attempts are being made at representing the interaction, at the molecular level, between cations and organic macromolecules (FALCK, 1988). A review of work in this area was produced and shows that three possible types of models are considered :

- discrete ligand models : they model the distribution of cations/protons between organic and inorganic ligands using stability constants as in usual speciation codes ; random-structure models are used for the molecular structure of the ligands ;
- continuous distribution models, which are able to interpret experimental titration curves with simple functions (e.g. Gaussian function) depending on only a few parameters ; they can only be used for interpolation ;
- surface complexation models, which assume that the ligand is more or less solid, and not affected by the chemical bonding ;

this could apply to very large molecules.

It is envisaged to incorporate such models into the PHREEQE code ; at present, a discrete ligand approach with a modification of the association constants due to electrostatic forces applying the surface complexation theory is developed.

It is worth noting that stochastic modelling of heterogeneous porous media is also tackled at the BGS, using a fractal approach in 2 dimensions.

2.2.3. Model development at Harwell, UK

In the area of far-field modelling of radionuclide migration, the model development work at Harwell is progressing along 5 different lines (PORTER, 1988 ; PORTER and WINTERS, 1989, contract 78). The first one is to test improved methods for solving non linear problems. In NAMMU the classical NEWTON-RAPHSON algorithm is used ; this can be very expensive to run, particularly when small meshes and a large number of nodes are required, e.g. for simulating brine flow with very large density differences, as was shown by the RIVM. Several other numerical methods are tested (quasi-Newton, modified Newton, Broyden, and Broyden-Fletcher-Goldfarb-Shanno). Only the Broyden method was found to provide a converged solution, while requiring only 40 % of the Newton-Raphson CPU time, for a problem of 6724 unknowns. Its relative efficiency would increase further with a larger problem. An additional increase in efficiency may be obtained by coupling the Broyden method with parameter stepping, as is at present being investigated. The Broyden method is a quasi-Newton method, in which the updating of the inverse of the Jacobian matrix of the system is made only in the direction of the update of the solution vector, see e.g. PORTER, 1988.

The second task is to incorporate chemical reactions into the NAMMU code. The current version only incorporates the linear equilibrium isotherm (K_d) approach. A first improvement was to allow the sorption of one species to depend on the concentration of a second, and also to use non-linear isotherms, where the concentration sorbed on to the solid is non-linearly related to the concentration in solution. Secondly, a ternary heterovalent ion exchange model, as described e.g. by VALOCCHI et al. (1981), was

introduced into NAMMU. This involves the simultaneous solution of 3 transport equations and the calculation of the sorbed concentrations, taking into account the cation exchange capacity of the medium and the competition between the cations as expressed by selectivity constants.

Testing and validation of this approach are currently in progress. Later on, it is anticipated that a full coupling of NAMMU with a geochemical equilibrium code such as PHREEQE could be carried out, as was done at Harwell in CHEQMATE (SHARLAND et al., 1986), a 1-D code for near-field transport that is taking part in the CHEMVAL intercomparison study (see section 2.3). It is worth noting that such direct coupling has already been investigated e.g. by D. NOY at the BGS, and found impracticable (NOY, 1986). However, a more efficient technique using the concept of chemical components to couple the transport code METIS with an especially constructed geochemical equilibrium code, CHIMERE, was used in France to produce the coupled code STELE (COUDRAIN-RIBSTEIN, 1988). The same approach could be tested with NAMMU.

Task 3 is the development of a new numerical method to simulate the advance of sharp fronts. This problem is investigated by Prof. P. ROE and co-workers at the College of Aeronautics, Cranfield Institute of Technology UK, using methods developed to simulate shock waves in aeronautical engineering. The most promising technique under investigation is called ROE's superbee (ROE, 1986). Accurate results in 2-D have been obtained without any spurious oscillations, even in cases with regular meshes with Peclet numbers of 200. The extension to irregular meshes and to media with sharply contrasting hydraulic properties is under way. The superbee method incorporates non-linear feedback into the flux terms (advective and diffusive) in order that in the final step all interaction terms be computed at the second order in time. The MUSCL scheme (VAN LEERS, 1979) is another means of achieving this objective. A progress report on these techniques is due in mid 1989.

The 4th task is an investigation of the use of stochastic modelling to analyse solute transport in heterogeneous porous media. This task is entrusted to the Department of Civil Engineering of the University of Newcastle upon Tyne, Dr. R. MacKay and Dr. R. Glendenning. After a survey of the literature dealing with stochastic modelling, a 3-D stochastic model was developed, in a cubic domain of 3 x 3 x 3 m including 27,000 elements 0.1 x 0.1 x 0.1 m in size. The log-hydraulic conductivity in the domain was

assumed to have a Gaussian distribution, with a spheric covariance model and a range of 0.5 or 1.5 m. The classical finite difference flow equation was then solved for 20 different realizations of the medium, obtained by Monte-Carlo simulations. The velocity field was calculated for each realization and transport was represented by particle tracking along the trajectories (advection with the velocity plus random anisotropic micro-dispersion). 1000 particles are used, starting from the same injection point in the domain.

For this ensemble of random fields, the mean position of the particles as a function of time is calculated, as well as their covariance, which represents macro-dispersion. The skewness and kurtosis of the particle distribution is also analysed. At present, the main findings are :

- there is little evidence for convergence towards a normal distribution of the particles over the time and distance considered in the study, meaning that transport at this scale is non Fickian ;
- the normal distribution is a good approximation for $t \rightarrow 0$;
- the non normality at later times (positive skewness, heavy tails) decreases if the range of the covariance of log-hydraulic conductivity, or the flow rate, increases ;
- for small velocities, the longitudinal component of the covariance function of the particle position, which represents dispersion, grows more than linearly with time, while the transverse component grows approximately linearly. This non linearity is reduced if the flow velocity is larger.

These findings are closely related to the work performed by DIEULIN (1985) in an earlier phase of MIRAGE. It is however not yet clear what final conclusions should be drawn for the representation of transport in heterogeneous media. The stochastic methodology is available, although very demanding in computer resources. For early times, it is clear that the equivalent deterministic models are inappropriate. For large times and large displacement distances, these models may be acceptable. For intermediate scales, artefacts such as changing dispersivities in deterministic models may improve their potential, but this remains to be established. A progress report on this work is expected towards mid 1989. It is also worth noting that the University of Newcastle is looking into the development of averaging rules for scaling up heterogeneities, a problem which is being tackled by many researchers in this area at present (e.g. JOURNEL et al., 1986 ; MARSILY

within the CEC (COSA, CHEMVAL), or elsewhere (INTRACOIN, HYDROCOIN, INTRAVAL) have always shown that many discrepancies between codes, or errors, were simply due to elementary mistakes in the introduction of the data in to the codes, thus pointing out the need for QA/QC procedures to eliminate such mistakes. See for instance KNOWLES and LOWE, 1986.

One must emphasize that QA/QC procedures should systematically be applied to all modern research activities and not only to modelling : in fact, it is most probable that in the near future, non QA/QC research will not be considered acceptable in any internationally funded research programmes.

However, let us focus here on modelling, which is the topic of this review. QA/QC techniques have been designed especially for modelling and even theoretical research in some institutions of the EC. Furthermore, G specific project called REQUEST, of the CEC ESPRIT programme on information technologies, specifically aims at increasing the reliability and quality of industrial software (CEC, 1987). It is also certain that, in the near future, normative institutions such as ISO will produce QA/QC standards in many fields, including modelling.

At this stage, it is too early for the Commission to request from its contractors that they adopt a uniform QA/QC plan, but it seems not too early to suggest that, for future contracts, a QA/QC procedure be submitted to the Commission by each of its contractors, at their initiative, for the Commission to review and possibly accept. This is, at present, a suggestion, which could be discussed at this MIRAGE plenary session, to be implemented during the next MIRAGE phase, after 1990.

It must, however, be realized that QA/QC procedures carry an additional cost, which in, the end, will have to be covered by the CEC or its associated member states. This reviewer strongly believes that "reasonable" QA/QC procedures are very cost-effective, and that this additional expense would be well worth paying for.

3. CONCLUSIONS AND RECOMMENDATIONS

The final conclusions will be completed after the discussions in the MIRAGE Plenary session, March 16-17, 1989. Only a few tentative suggestions are given below.

(i) It appears that the MIRAGE project has become, over the years, better and better coordinated. This involves better coordination and cooperation between the modellers, but also better coordination between the various research areas of MIRAGE, i.e. laboratory work/in situ measurements/ analogues.

(ii) Whereas modellers seem to be more or less able to handle experimental data produced in the laboratory (on plugs, columns...), they realize today that applications and validation in the field will in general be extremely complex and data demanding.

In many of the studies described above, "uncertainty" becomes the major word. Quantifying these uncertainties (e.g. with stochastic modelling) for a certain level of reconnaissance of the environment may be one of the most important aspects of the next MIRAGE project. Some early research has already been done along this line, inside or outside MIRAGE.

(iii) If uncertainties can be ascertained or bounded, the next question is then whether acceptance criteria are available to deal with these uncertainties. This extends beyond the area of radionuclide transport in the geosphere, as was shown by the results of the COSA exercise on rock mechanics computer codes, KNOWLES and LOW (1989) but needs to be addressed somewhere in the radioactive waste disposal programme.

4. REFERENCES

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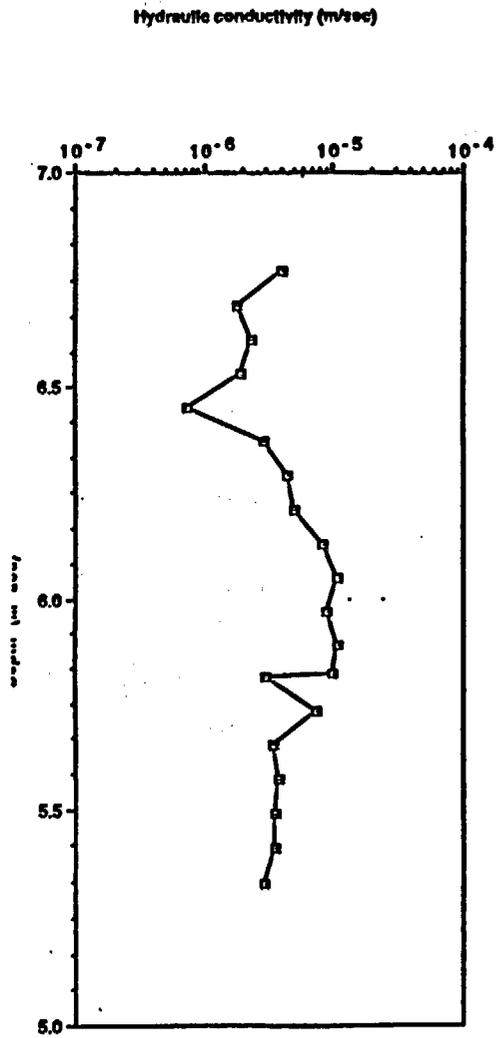
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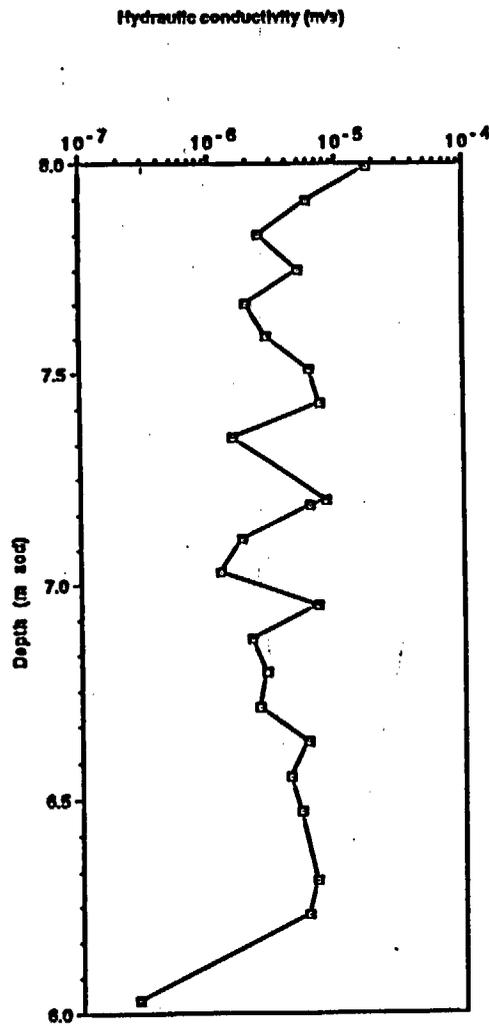
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Borehole D207



Borehole D205

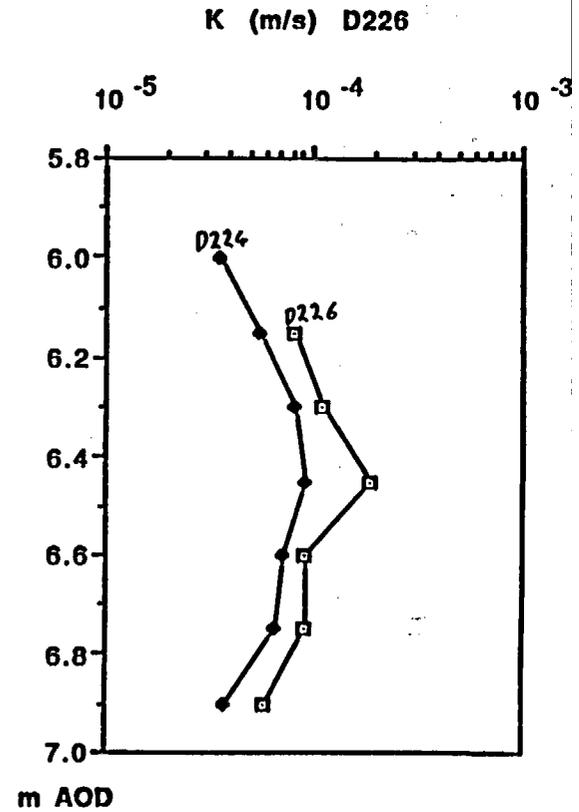


Figure 1 : DRIGG experiment (from BGS, UK)
 Measured hydraulic conductivity in two boreholes, an estimated conductivity from the interpretation of the tracer tests

2-dimensional numerical

port 10

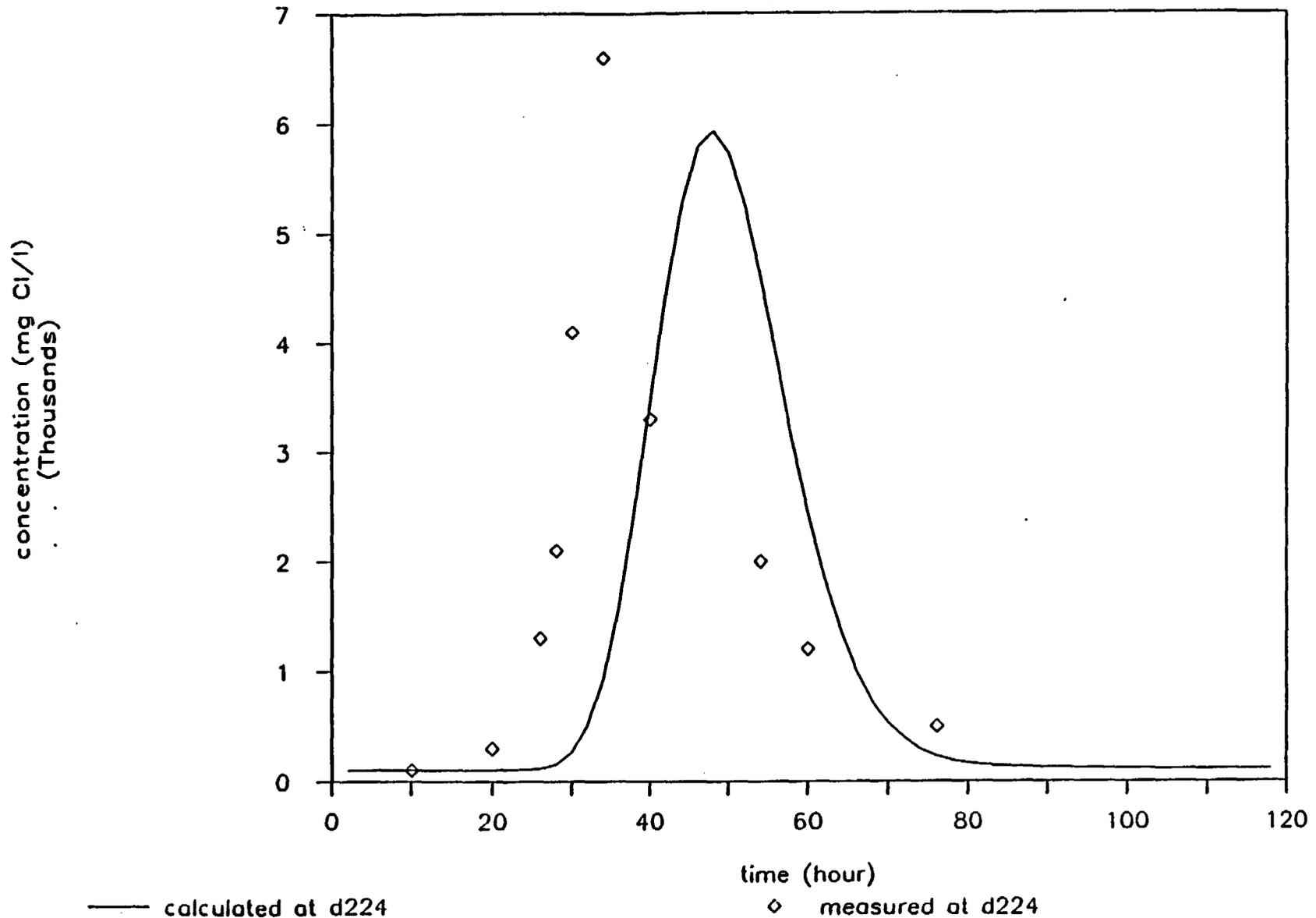


Figure 2 : DRIGG experiment (from Delft Geotechnics, NL)
Comparison of the calculated and measured breakthrough curves at a given level,
based on the measured hydraulic conductivity, without fitting

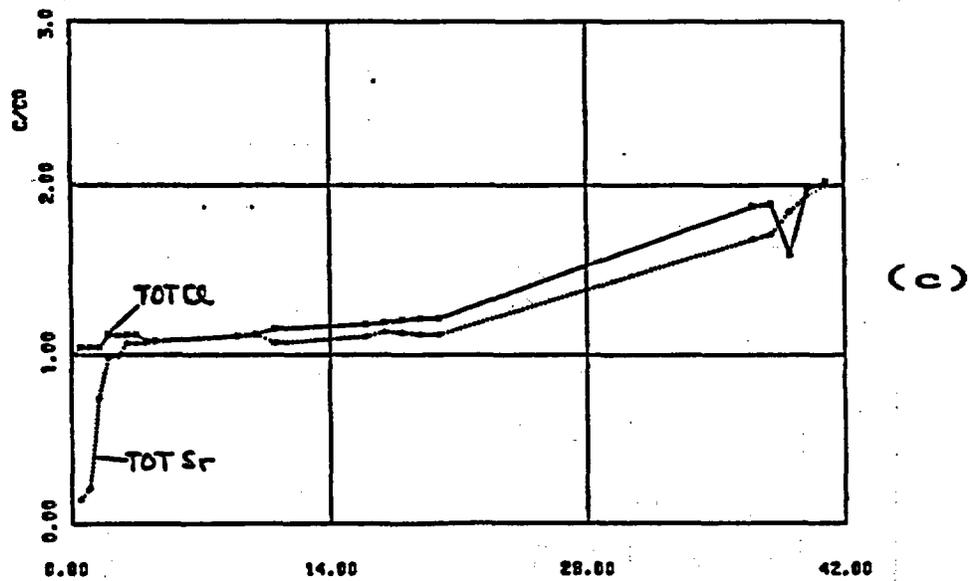
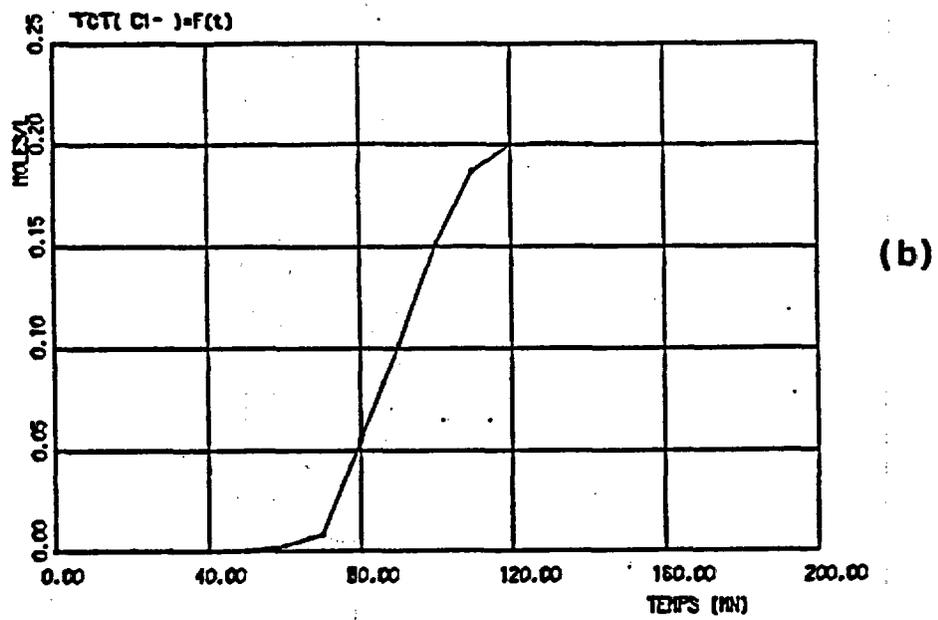
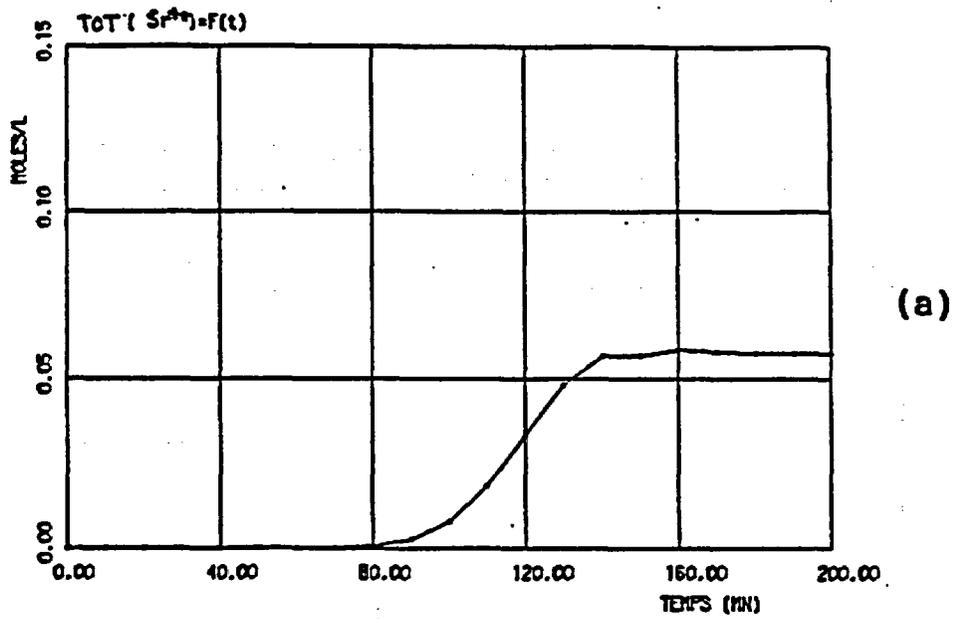


Figure 3 : Coupled geochemical transport (from EMP-CEA)
 Calculated breakthrough curves for Sr²⁺ (a) and Cl⁻ (b)
 and observed curves (c) on the column experiment

ALICE - VERSION DU 11.10.88

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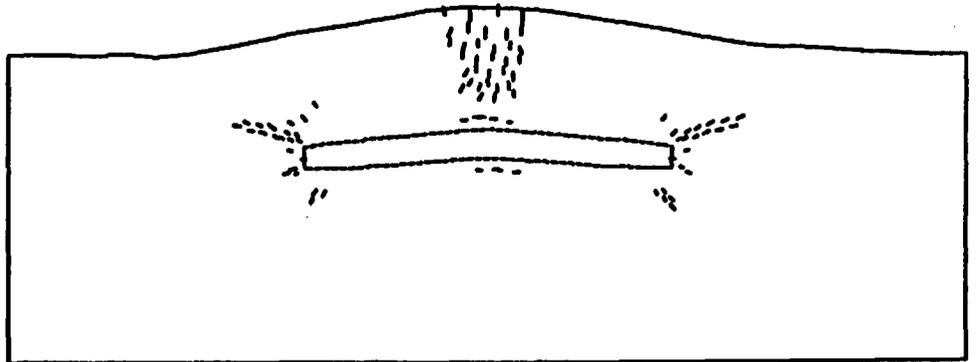
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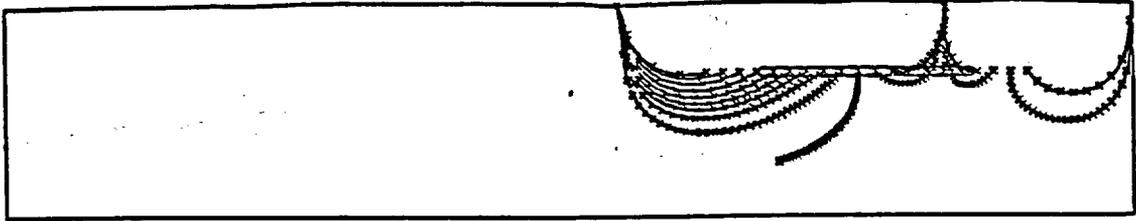
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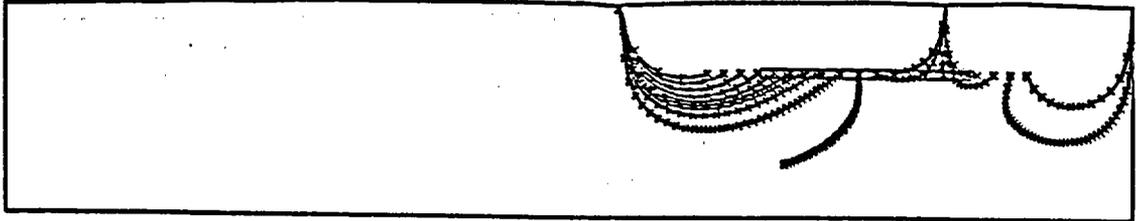


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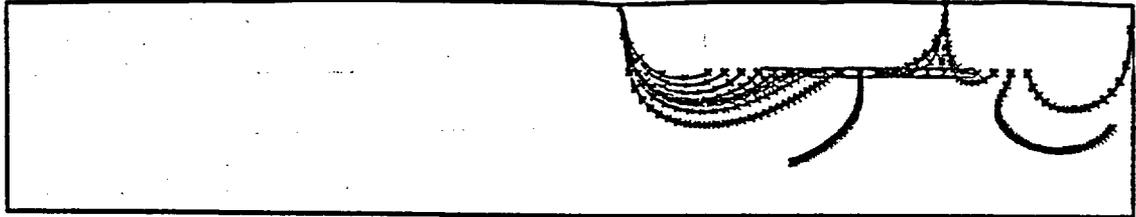
Figure 5 : Flow path in crystalline rocks (from CEA-ANDRA-DEMT)
Trajectories of particles released from the center of the repository,
at times ranging from 5000 y (top) to 2000/1000/600/150/0 (bottom).
For each case, a travel time of 50,000 years, with an x each 1,000 years



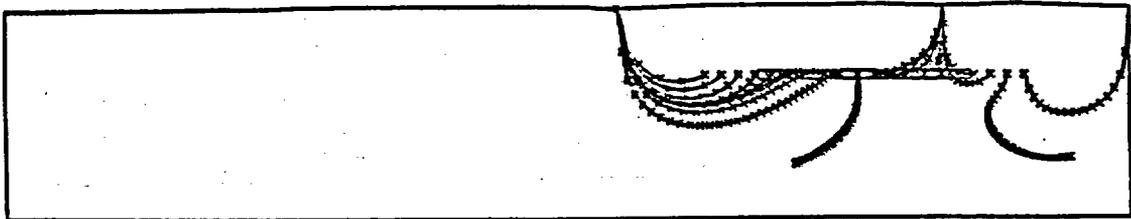
TRAJECTOIRES-RD VARIABLE-T0=5000-TMAX=50000 (1000ANS ENTRE X)



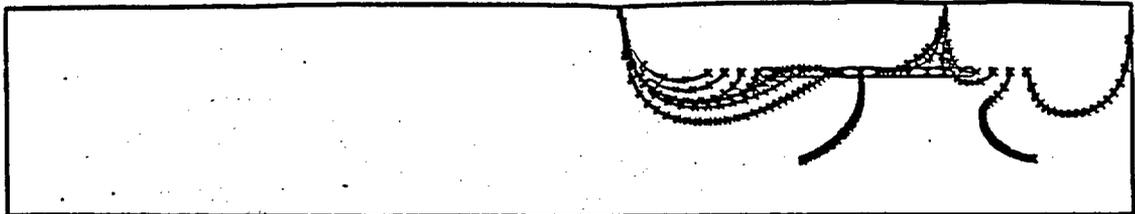
TRAJECTOIRES-RD VARIABLE-T0=2000-TMAX=50000 (1000ANS ENTRE X)



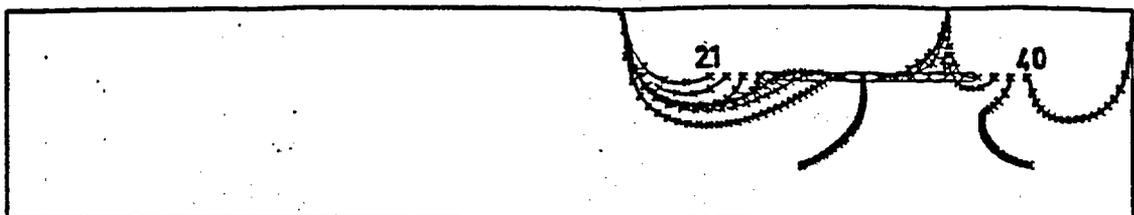
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TRAJECTOIRES-RD VARIABLE-T0=600-TMAX=50000 (1000 ANS ENTRE X)



TRAJECTOIRES-RD VARIABLE-T0=150-TMAX=50000 (1000 ANS ENTRE X)



TRAJECTOIRES-RD VARIABLE-T0=0-TMAX=50000 (1000 ANS ENTRE X)

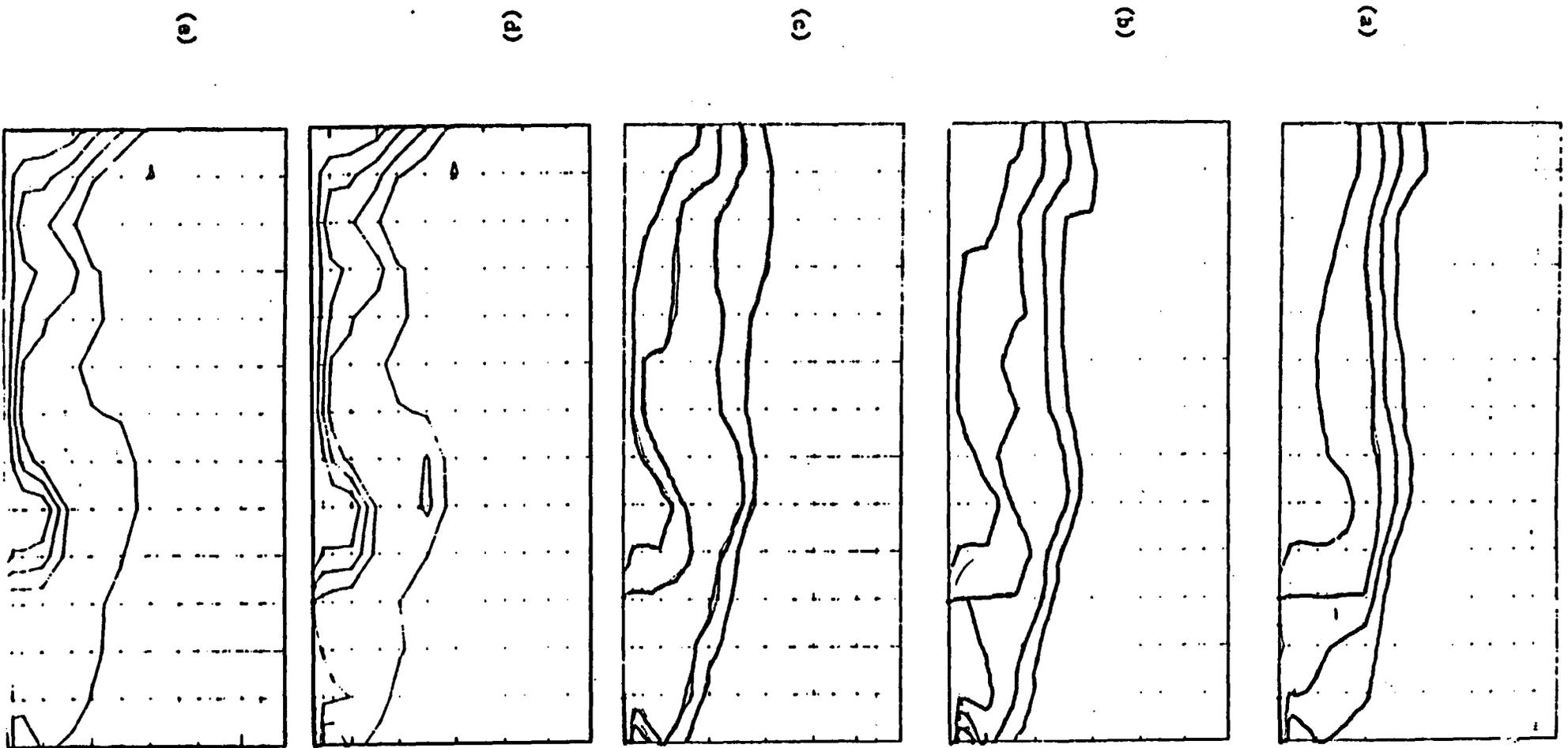
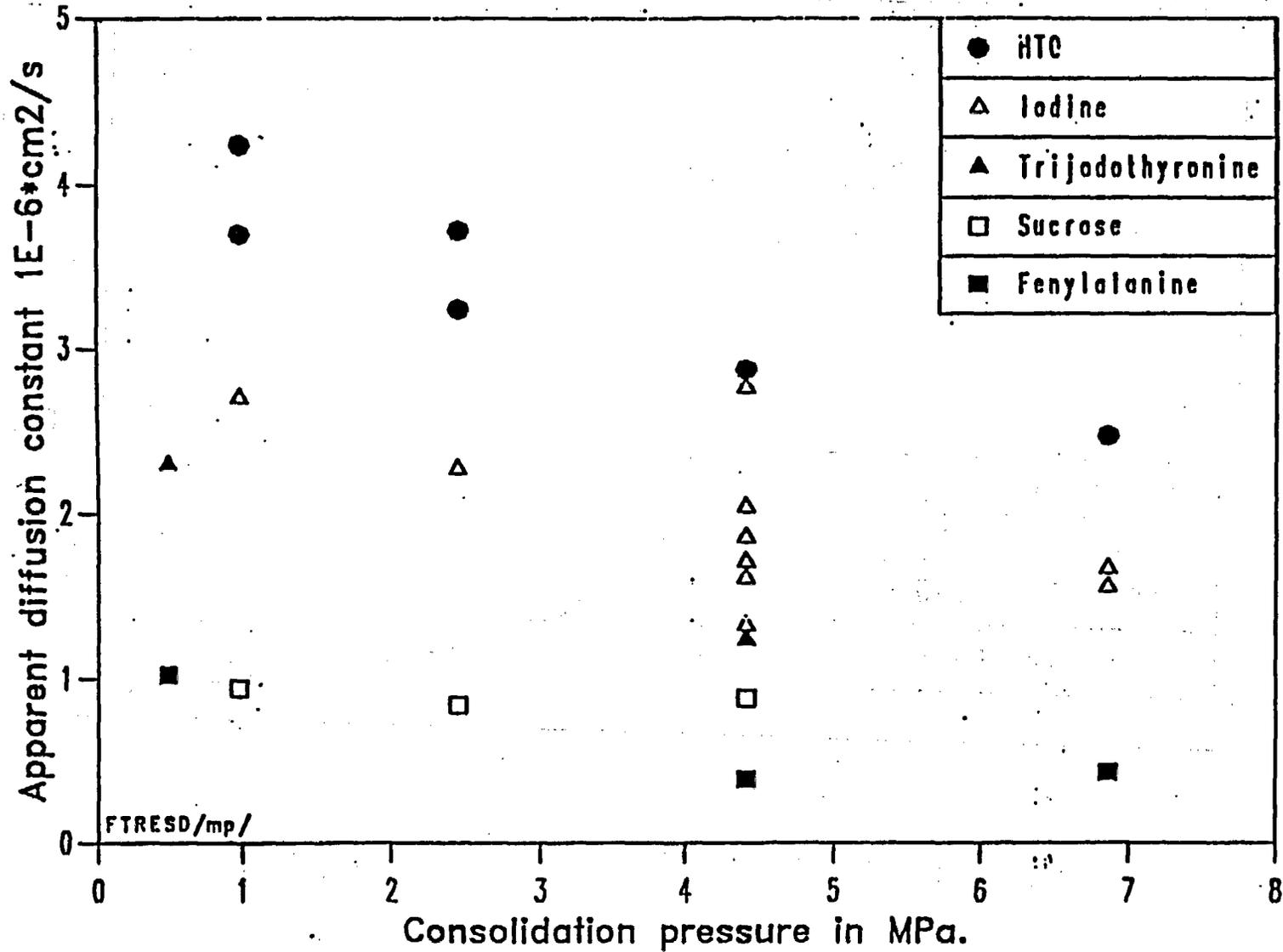


Figure 6 : Salt concentration profiles above the Gorleben site (from RIVM)
calculated with METROPOL after 100 y (a), 500 y (b), 1000 y (c), 2000 y (d) and 3000 y (e)



Influence of consolidation pressure on apparent diffusion constant.

Figure 7 : From CEN-SCK
Through-diffusion experiments on clay plugs

Migration experiment with Tc (cell 5)

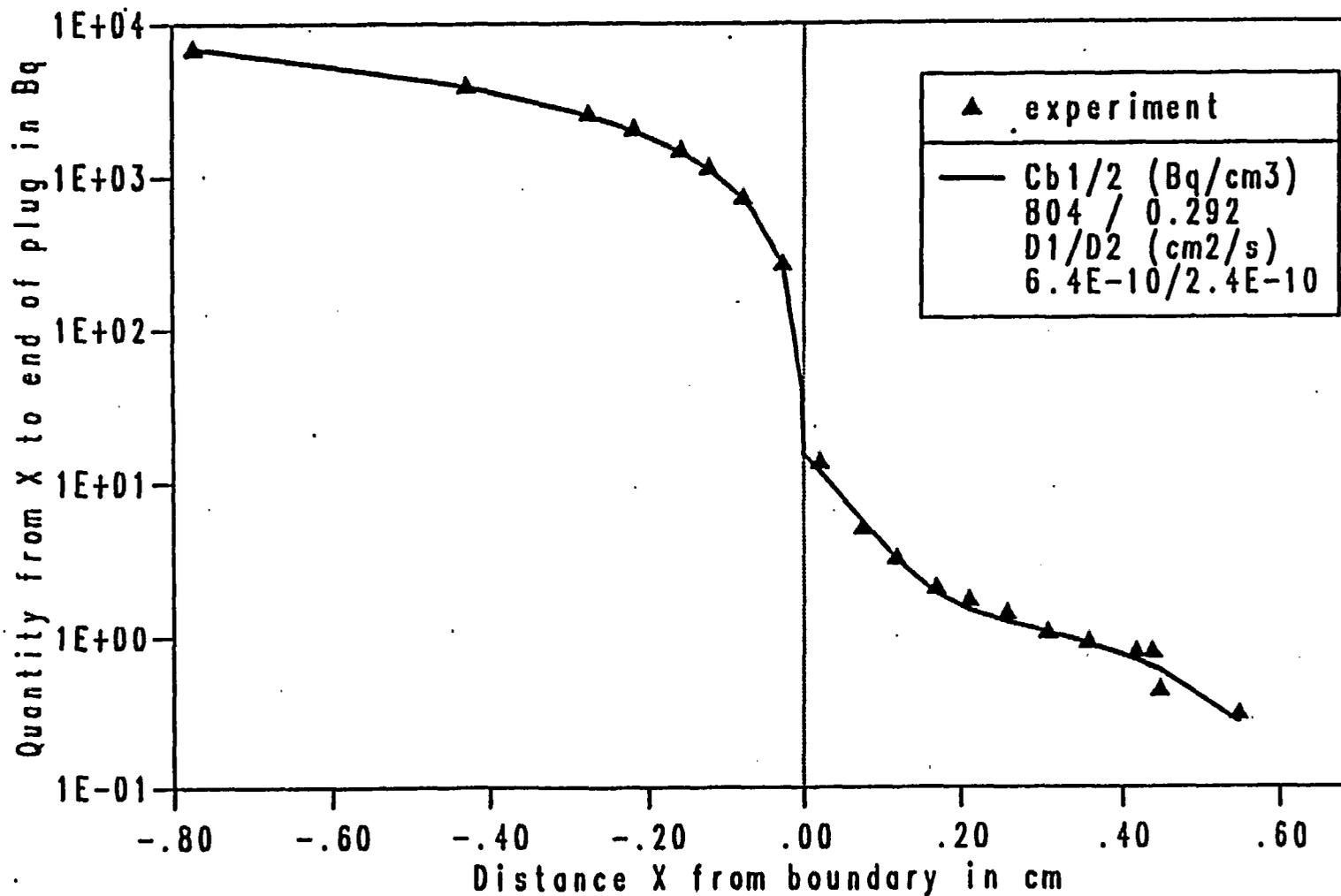
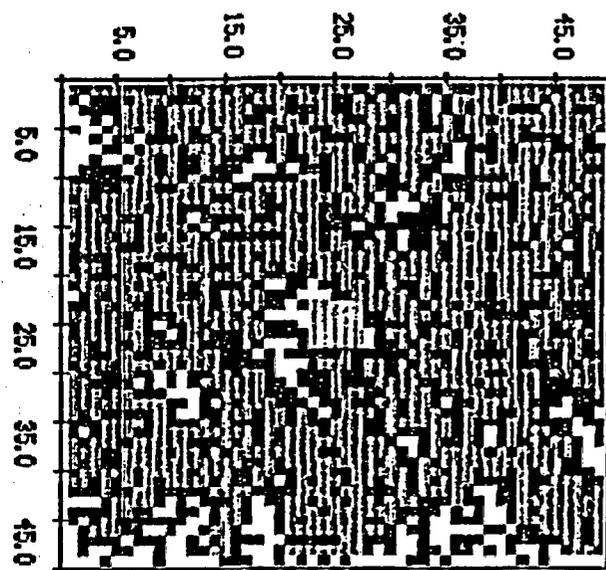


Figure 8 : From CEN-SCK
Diffusion experiments by contacting clay plugs

DIF ← 2D



DIF ← 2D

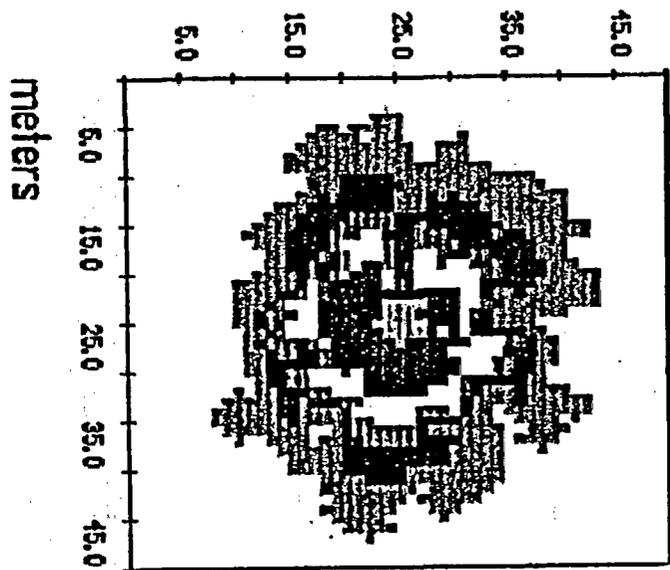
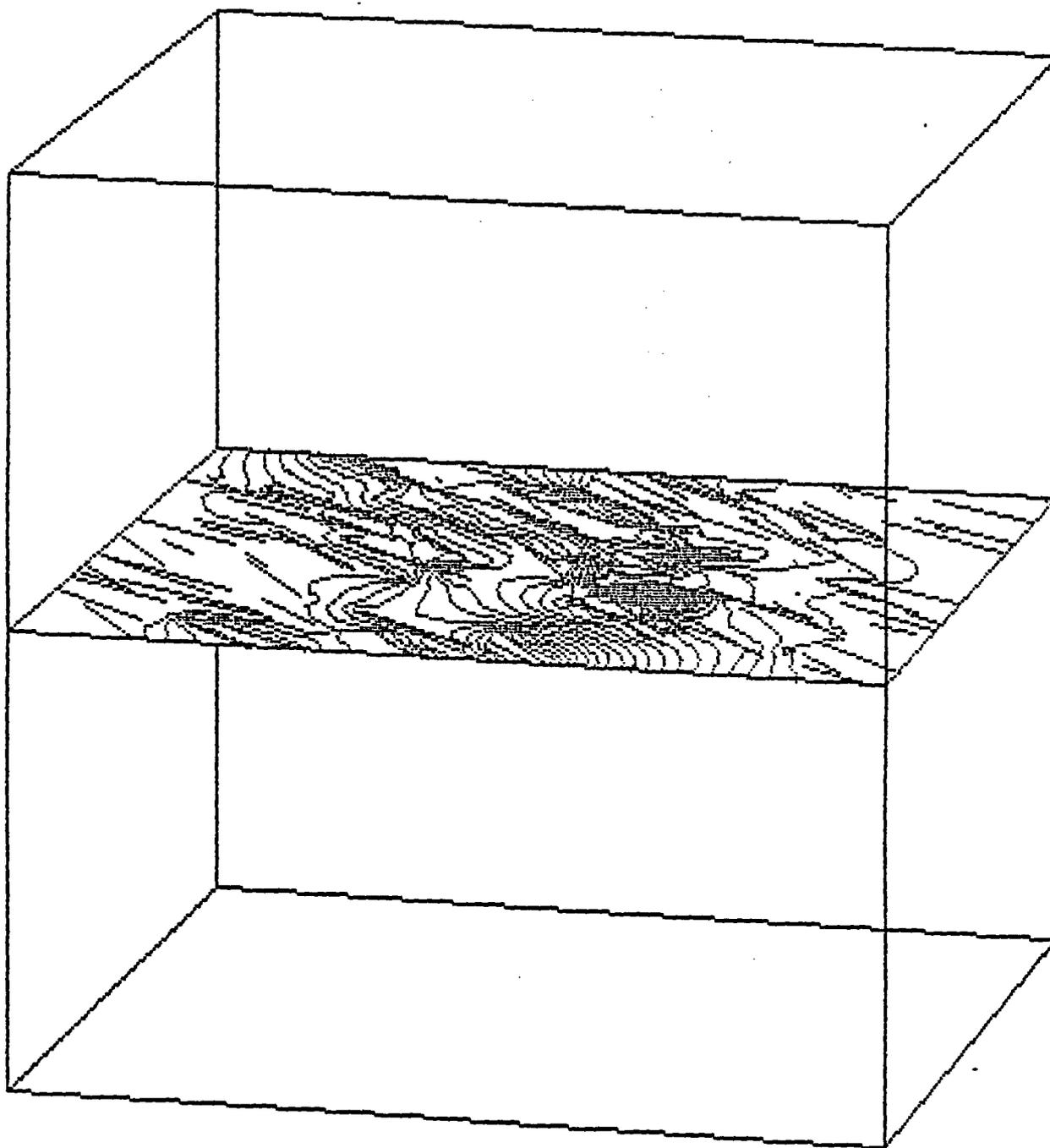
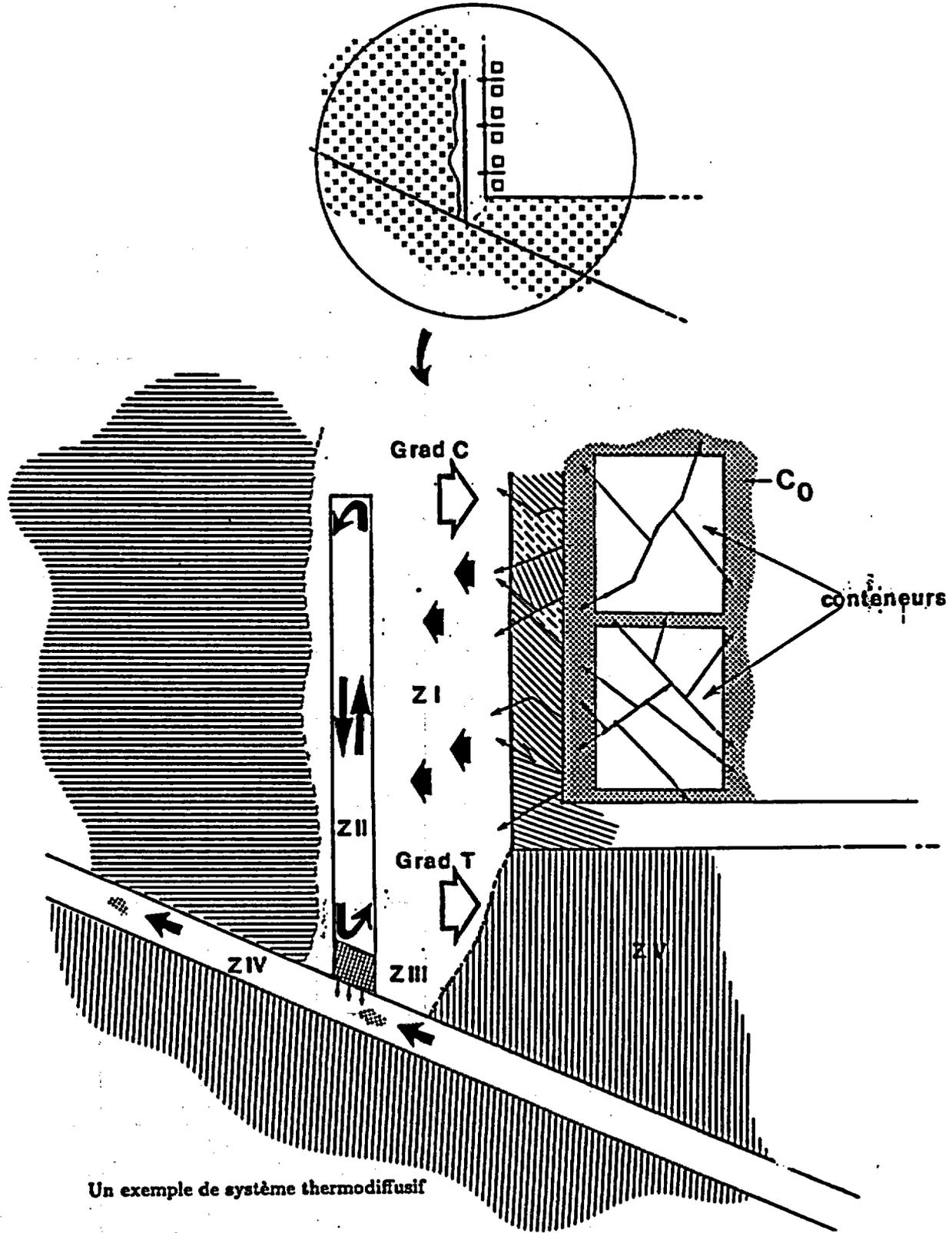


Figure 9 : From RISØ
Random field and stochastic numerical diffusion experiment



**Figure 10 : From UKAEA-Harwell
Flow in a fracture plane in NAPSAC**

Transferts non dominants

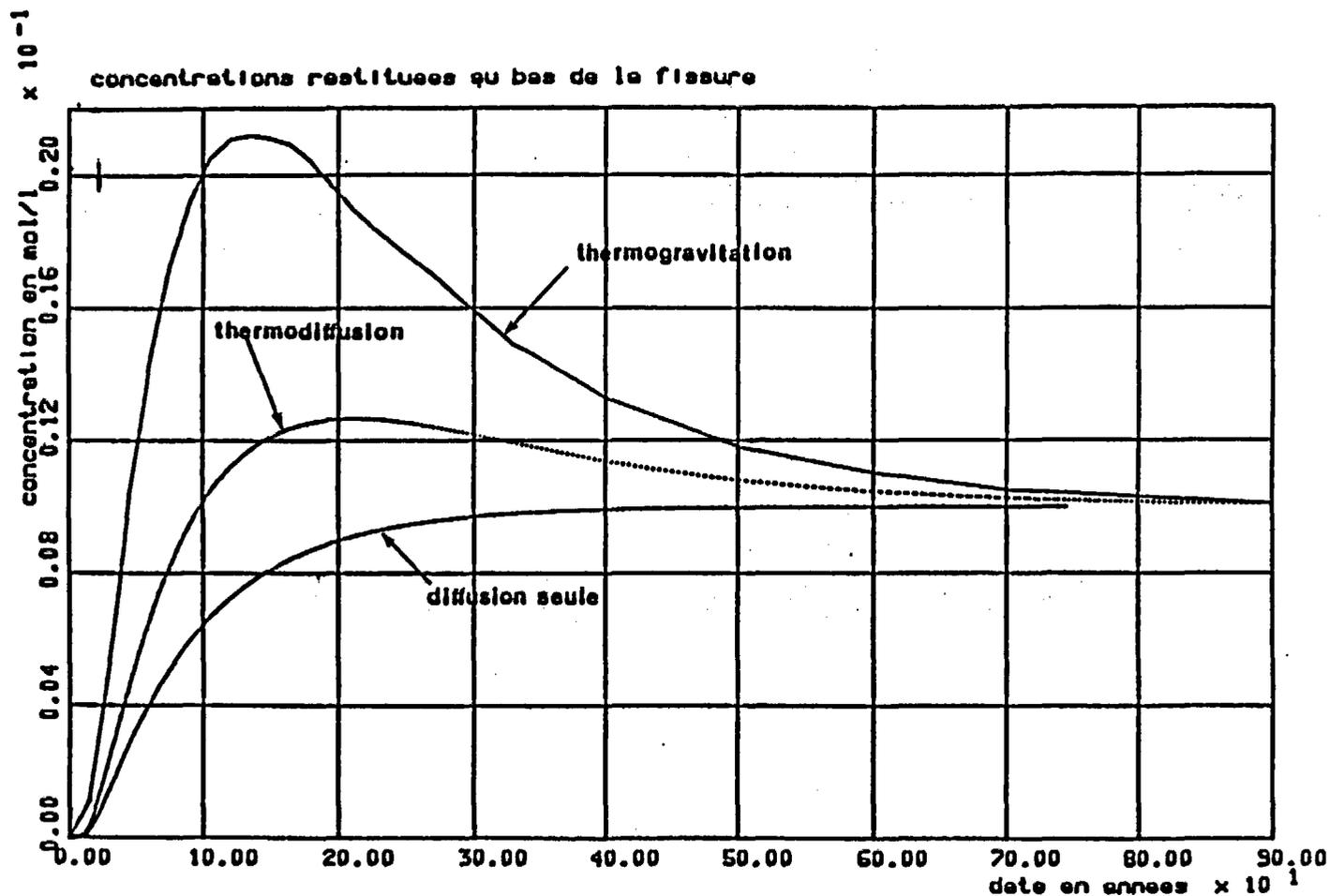


Un exemple de système thermodiffusif

Ecole des Mines - CEA/IPSN/DAS

Figure 11 : From CEA-EMP
Set-up for example of thermogravitational effect

Transferts non dominants



Effet thermogravitationnel, concentrations calculées

Figure 12 : From CEA-EMP
Comparison of pure diffusion, thermal diffusion and thermogravitation
for the theoretical example

ATTACHMENT 4

The CHEMVAL Project : Status Report, March 1989

D. Read and T.W. Broyd

WS Atkins Engineering Sciences, Epsom, Surrey, UK

Presented at a Plenary Meeting of the CEC MIRAGE
Project Co-ordinating Group, Brussels, March 1989

SUMMARY

This paper summarises the progress made during the second year of CHEMVAL, a three-year project concerned with the verification and validation of computer programs describing the chemistry of radioactive waste disposal systems. Seventeen organisations from eight countries are participating in CHEMVAL, which is being undertaken within the framework of the Commission of European Communities MIRAGE 2 programme of research.

1. INTRODUCTION

Estimation of the long-term health risks arising from radioactive waste disposal requires the use of predictive computer programs capable of quantifying the effects of significant release, transport and immobilisation mechanisms. The majority of programs in use today assume system equilibrium when calculating radioelement speciation/solubility and rely on extensive thermodynamic databases for both major constituents and elements of environmental concern. Whilst some preliminary work has been undertaken on the verification of such equilibrium codes and data [1,2], relatively little effort has been expended on model validation; that is confirming that the models accurately represent the behaviour of the chemical system being simulated. In addition, the more sophisticated models which couple chemical equilibria with hydrodynamic transport have yet to be considered.

Attempts to address the above form the basis of the international CHEMVAL project [3] funded jointly by the Commission of the European Communities (CEC) and the United Kingdom Department of the Environment (UKDOE). The work forms part of the CEC MIRAGE2 programme of research [4].

Within CHEMVAL, aspects of model verification/validation involve the active participation of fourteen research organisations from European Community member states, Finland, Switzerland and Sweden (Figure 1). Together they perform co-ordinated studies designed to increase confidence in chemical speciation and transport modelling. The remainder of project resources are devoted to reviewing,

extending and improving the body of thermodynamic data available to participants, concentrating on those elements of greatest perceived relevance to radiological assessment [3].

The CHEMVAL project consists of four main stages:

STAGE 1 : application of aqueous speciation codes to representative cement water and groundwater compositions.

STAGE 2 : attempts at validation of aqueous speciation models by comparison with experimental field and laboratory data.

STAGE 3 : verification of coupled chemical transport codes.

STAGE 4 : attempts at validation of coupled models against experimental data.

Stage 1 is now complete [5], Stages 2 and 3 are nearing completion and Stage 4 commenced in February 1989. This paper summarises progress made on each of the above stages together with database work during the second year of CHEMVAL. The current programme of research will run until 1990.

2. CHEMVAL STAGE 1 - MAIN FINDINGS

Owing to the large number of codes and associated thermodynamic databases available to CHEMVAL participants [1,5] an extensive verification exercise was felt to be essential prior to attempting validation studies. This first stage was intended to provide a common reference point among European organisations by:-

- i) highlighting differences in thermodynamic data used at each organisation and the importance of such differences in determining radioelement speciation and solubility.
- ii) assessing the ability of computer codes to cope with realistic radioactive waste disposal problems.

iii) confirming areas where further work is needed to improve both programs and supporting data.

An agreed methodology was adopted for the verification study in order to distinguish variation in results caused by differences in thermodynamic data from that caused by other factors such as coding errors or procedure [5]. Participants were asked to perform calculations first with their own "in-house" data and then to repeat the simulations with a standard CHEMVAL Database [3] distributed in June 1987. This preliminary listing contained formation constants for 376 aqueous complexes and solubility products for 259 solids (Table 1).

Test cases, based on actual field or laboratory analyses, focussed on a cementitious "near-field" and two alternative "far-fields"; clay aquitard - sandstone aquifer and granite host-limestone aquifer. Roughly six simulations were devised for each of the five systems ranging from relatively simple base case problems of aqueous speciation to complex reaction path calculations involving solution mixing and "irreversible" oxidation or reduction. The radioelements included were americium, plutonium, uranium, technetium, caesium strontium and cobalt.

Sufficient results were obtained to demonstrate that all five of the codes used in the exercise were capable of solving the wide range of geochemical problems set [5]. No serious "bugs" were identified in the computer programs, PHREEQE [6], MINEQL [7], EQ3/6 [8], WHATIF [9] and CHIMERE [10], though each has its shortcomings. In the case of PHREEQE [6], for example, problems may be encountered owing to pH drift and options for activity coefficient correction or treatment of alkalinity. These are discussed in detail elsewhere [5].

Though, in the main, excellent agreement was obtained not only for straightforward speciation calculations but also for conceptually difficult reaction path problems, several sets displayed a lack of consistency. In those instances, variation in the results has been ascribed to the following, in decreasing order of frequency:-

- constants included in, or omitted from, the database.

- operator decision, either with respect to the database (e.g. choice of solubility limiting phase) or procedural (e.g. fix or "float" pH).
- limitations of extent software.

Considerable effort was made during CHEMVAL Stage 1 to isolate discrepancies caused by differences in thermodynamic data. The more important of these are highlighted in Table 2 and are regarded as priority areas for future research. For further information on the verification study the reader is referred to the accompanying CHEMVAL Stage 1 report [5].

3. STATUS OF CHEMVAL STAGE 2

i) Procedures

Whereas the verification exercise described above considered realistic but largely hypothetical test cases, Stage 2 is concerned with the performance of equilibrium codes and data when simulating real field and laboratory data sets. Following review, a dozen candidate sites were reduced to a shortlist of four, based on data availability and relevance to radiological risk assessment:

Mol - a prospective repository in organic-rich clay

Gorleben - actinide solubility experiments on groundwaters taken from above the potential salt repository

Maxey Flats - an existing near surface low level waste facility

Oman - highly alkaline spring waters, loosely representative of a cementitious near-field.

Nineteen test problems of varying complexity (Table 3) were formulated and distributed to participants in May 1988. Wherever possible an attempt was made to allow quantitative comparison between the results of modelling and experimental measurements.

However, as none of the above sites has yet been fully characterised this was not a realistic aim in all cases and no more than qualitative comparisons can be drawn. Initially, the results of "blind predictions" were requested, allowing individuals complete freedom of choice with respect to the codes and databases used. Following receipt of the results, experimental details were provided in order that participants refine their simulations, where necessary, to improve correspondence with experiment. Finally the researchers who had been involved in the experimental studies were invited to a meeting to discuss the accuracy and, in some cases, suitability of the models employed. An assessment is now being made of model performance and the extent to which the codes and databases could be considered to have been validated.

Before discussing the results, note is made of the term "validation" as used here. Given the uncertainties inherent in natural system studies, complete validation of computational methods can rarely, if ever, be achieved. Within the context of the CHEMVAL project validation is taken as qualitative or quantitative evidence that the models accurately reflect laboratory or field observations. Naturally, more credence is attached to correct prediction of trends than coincidental agreement of point values.

Examples from the Mol and Gorleben studies are given below.

ii) Preliminary Results

a) Mol

The Tertiary Boom Clay at Mol has been studied for many years but only since 1984, when an underground experimental facility was excavated have accurate geochemical data been obtained. Originally, the clay was regarded as a simple inorganic cation-exchanger but it is now known that under in-situ conditions inorganic ion-exchange reactions have much less effect on radioelement solubility and speciation than organic complexation [11].

The mineralogy of the Boom Clay is well known and representative analyses of water from the clay and adjacent aquifers have recently been published [11]. They show the clay water to be alkaline and

strongly reducing. Details of experiments to characterise the organic matter present are also available. To date, however, measurements of actinide solubility have been reported only for "synthetic clay water" and the latter was used in conjunction with actual interstitial water during the formulation of test cases.

Five separate exercises were designed to investigate processes known, or thought, to be operating in the Boom Clay. They include pH buffering, redox poisoning by iron sulphides and irreversible oxidation of the clay on exposure to air (Table 3). Most interest within the CHEMVAL group has focussed on the results of actinide solubility modelling.

The majority of participants chose the CHEMVAL Stage 2 Database (Table 2) for this study, accounting for the generally good correspondence in reported results. In the case of simulations on synthetic clay water, predicted solubilities for the actinides are also in close agreement with experiment (Figure 2). The solubility of both americium, at equilibrium with $\text{AmOHCO}_3(\text{s})$ and neptunium, constrained by $\text{Np}(\text{OH})_4(\text{am})$, are within a factor of three of the measured values in all cases. Measured plutonium concentrations fall between those predicted for equilibrium with $\text{PuO}_2(\text{c})$ and $\text{Pu}(\text{OH})_4(\text{am})$, consistent with the findings of Stage 1 [5] and the known ageing behaviour of Pu(IV) hydroxy polymer [12]. For this simple experimental system and in the absence of organics, the use of the $\text{Pu}(\text{OH})_4(\text{am})$ results in a radiological assessment would provide a conservative estimate of plutonium solubility.

Although the above findings are encouraging they cannot be extended to the field situation at present. No direct actinide solubility measurements have yet been performed on actual clay waters, rich in humics. However, it is known from parallel experiments on europium that complexation by humic substances is likely to be nearly quantitative in the Boom Clay [11]. This is not reflected by the modelling studies carried out to date which show little uptake by organic ligands, owing to hydrolysis and carbonate binding (Figure 3). The discrepancy is not thought to be merely a function of inadequate data but rather a consequence of the fundamental inadequacy of simple ion-association models for representing complexation by natural organics.

b) Gorleben

The Gorleben salt dome was designated a provisional site for solid radioactive waste disposal in 1977. Since then, the geochemistry of much of the dome and overlying sediments has been characterised, largely as a result of work undertaken at the Technical University Munich (TUM). Actinide solubility has been measured in groundwaters and synthetic saline solutions after conditioning with rock samples taken at various depths. Recent data are available for plutonium, americium and neptunium [13]. Perhaps the most significant aspect of the work has been the identification of actinide colloids, even at high salinity, emphasising the importance of solid-liquid phase separation during analysis. Fortunately in a number of cases TUM have reported solubility as a function of filter size down to 1nm.

Analyses of actual Gorleben groundwater, showing an increase in salinity with depth, were used to construct the test data sets. The waters have a pH close to 7 and are all slightly oxidising. Processes addressed during CHEMVAL Stage 2 include the solubility of americium, plutonium and neptunium together with actinide complexation by EDTA and citrate. Owing to uncertainties concerning the correction of activity coefficients in strongly saline solutions, only brackish waters were considered (ionic strength < 0.3).

Problems were anticipated with solubility calculations due to the known occurrence of organic and inorganic colloids in Gorleben waters. For this reason, ultrafiltered solution compositions were specified wherever sufficient information was available. Thus, in the case of americium, predicted solubilities in two of the model solutions are in extremely good agreement and close to the concentration measured in 1nm filtrate (Figure 4). By contrast, estimates for coarser (450nm) filtrates show some scatter and deviate from analytical levels by at least an order of magnitude. The discrepancy between experimental and calculated values is not easily predictable and, in the example shown, the models over- rather than under- estimate the concentration of americium in solution. This may be explained by the fact that although americium levels are higher in coarsely filtered water, owing to the presence

of colloids, concentrations of potential ligands are also higher. Including elevated analyses of the latter in the calculations accounts for the discrepancies observed (Figure 4).

A series of experiments have been performed at TUM to investigate actinide binding by EDTA and citrate [13]. Plutonium or americium spikes were added to 2nm groundwater filtrate and after one year's contact with Gorleben rock cores distribution coefficients (R_s) were measured as a function of ligand concentration. Modelling studies within CHEMVAL were designed to mirror this trend since as aqueous complexation increases, R_s should fall.

From Figure 5, it can be seen that one organisation (EMP) indicates a slight rise in the concentration of plutonium citrate complexes at the point where the ligand concentration exceeds 10^{-5} mol dm^{-3} . The other participant suggests citrate complexation is insignificant in this system. The experimental results lie between the two predictions (Figure 5). Measured R_s values do decrease somewhat at 10^{-3} mol dm^{-3} citrate but, without question, binding is weak and the models are qualitatively correct. The same may be said of the americium - EDTA experiments, all four organisations indicating quantitative complexation of americium by EDTA at ligand concentrations above 10^{-6} mol dm^{-3} (Figure 6). This is reflected in the experimental sorption data which show a rapid drop in R_s immediately EDTA is added to the solution [13]. Although the implications of the Gorleben study are still being assessed, the findings to date would seem to constitute positive, albeit indirect, evidence of equilibrium model validation.

Modelling carried out on the Maxey Flats and Oman sites have been omitted from this paper for reasons of brevity. Results will be described in detail within a report on CHEMVAL Stage 2 to be produced in Autumn 1989. Preliminary data for the Maxey Flats exercise appear promising with current models closely reproducing controlled oxidation experiments conducted on cement buffered and unbuffered trench leachates. The Oman study has proved to be less useful for model validation owing to uncertainties regarding field mineralogical and hydrochemical data.

In summary, CHEMVAL Stage 2 has demonstrated that equilibrium models can produce a reliable estimate of experimental data when used within their known frame of reference. It has also highlighted the limitations of current codes and data, though it would be inappropriate to dismiss the models for failing to reproduce field measurements in those cases where key processes are known to have been ignored. For example, plutonium solubility in the Boom Clay was simulated in terms of an inorganic precipitation reaction when clearly organic complexation is significant and immobilisation is a function of humate filtration [14]. Similarly, at Gorleben, solubility calculations cannot be expected to be accurate in unfiltered water owing to the presence of colloidal material.

4. STATUS OF CHEMVAL STAGE 3

1) Procedures

In contrast to standard speciation packages, coupled chemical transport codes are new, relatively untested and, in the main, poorly documented. Since the current work within CHEMVAL constitutes the first exercise of this type involving coupled codes, test cases were kept fairly simple and verification was approached in a stepwise manner.

Both direct (e.g. CHEMTARD [15], THCC [16]) and iteratively coupled codes (e.g. CHEQMATE [17], STELE [10]) were available for this work; the former incorporating mass action terms within transport equations, the latter relying on iteration between discrete chemical and transport packages. For this reason, it was decided to investigate the results obtained from such codes for the separate aspects of equilibrium chemistry and contaminant migration before proceeding with fully coupled problems. The processes addressed were:-

- a) Speciation - five cases based on CHEMVAL Stage 1 [5] and designed to test:
 - aqueous speciation in cement leachate
 - radioelement solubility in clay groundwater
 - redox equilibria

- sorption of caesium via an "ideal" exchange model
- sorption of uranium via surface complexation

b) Migration - six cases based on previously published MIRAGE work [1] and designed to test one-dimensional nuclide migration as a function of:

- boundary conditions
- aquifer properties (dispersivity etc)
- nuclide decay
- chain decay
- transport through multi-layered geospheres

Results have been collated for nine of the eleven cases and, where applicable, compared to analytical solutions. Examples are given later in this section.

In addition to the above, three coupled cases have been formulated to consider cement dissolution, bentonite alteration and actinide transport, respectively. The processes simulated in each case are summarised in Table 4.

In theory, the coupled codes employed within CHEMVAL are capable of performing most of the Stage 3 problems. Difficulties were anticipated however, owing to the disparate solution procedures used, particularly in the treatment of sorption processes, and thus the feasibility of the test problems needed to be established first. The results outlined below are preliminary and based on these feasibility calculations. More rigorous verification will follow once factors such as the use of different time-distance grids have been standardised.

ii) Preliminary Results

a) Chemical Models

The main objective of CHEMVAL Stage 3 is to test the flexibility and accuracy of coupled chemical transport programs rather than thermodynamic data. In view of this, participants used the Stage 1

version of the CHEMVAL Database throughout to allow direct comparison with the results of the speciation code verification exercise [5].

Sufficient data have now been collated for three of the five cases to allow meaningful comparison. Results are in extremely good agreement in all cases. Figure 7, shows the concentration of calcium species predicted by each organisation for a cement solution; a horizontal line parallel to the abscissa denoting exact correspondence. The use of a small subset of the CHEMVAL Database by the directly coupled code CHEMTARD [15] did not produce significant differences in computed speciation.

b) Transport Models

The six transport problems consider migration of a single nuclide or three-member chain through a one-dimensional porous medium with constant groundwater velocity. One variant case also addresses pure diffusion. The data produced may be compared to those reported during a previous MIRAGE verification exercise [1] which included the results of analytical solutions.

Preliminary results display close agreement and do not deviate significantly from those produced by the analytical code, GE01 [18]. Figure 8 shows the concentration versus time profiles produced by STELE [10], CHEMTARD [15] and GE01 [18] for transport of U-234 at a distance of 500m from the source. Uranium was released from an exponentially diminishing source at the inner boundary. It can be seen that both numerical codes accurately predict peak concentration and time.

c) Coupled Simulations

Results for calculations involving full coupling of chemical equilibria to hydrodynamic transport are, so far, available only for the cement near-field case (Table 4). This envisages the permeation of groundwater into a "cement" solution, slightly supersaturated with respect to portlandite (Ca(OH)_2). Transport is by 1-D

advection and results in dissolution of portlandite and precipitation of calcite along the flowpath. The effects of precipitation/dissolution reactions on porosity were ignored.

Figure 9 plots pH profiles at 200 years from which it is apparent that all three codes used predict a similar sharp increase in alkalinity close to the source. Even without optimisation of grid spacing or time-stepping, the results are highly encouraging from the point of view of verification. For example, the distance over which calcite precipitates after 400 years is predicted as 2.75m by CHEQMATE [17], 2.7m by CHEMTARD [15] and 2-4m by STELE [10], the last employing a much coarser time-space grid. These preliminary findings are to be refined during the period May-July 1989.

5. THERMODYNAMIC DATABASE ACTIVITIES

The compilation and review of thermodynamic data forms an essential part of CHEMVAL, and will continue throughout the duration of the project. Database activities are not performed in isolation but rather are driven by the core model verification/validation studies. This reflects an overall project requirement that a reviewed database be tested as thoroughly as possible against representative analytical data given the resources available. Thus, whilst the database work is being led by the Universities of Manchester and Wales [3], in effect all CHEMVAL participants contribute to the review work either through simulating the chemistry of field/experimental systems (Sections 2,3), independent literature review [19], or by performing sensitivity studies to investigate the effects of uncertainty in equilibrium constants for key species.

Work to date has led to the production of a standard CHEMVAL Database which is being updated at regular intervals during the project. The most recent version, issued in April 1988, contains constants for 521 aqueous complexes and 327 solids (Table 1) with emphasis placed on major groundwater components and radioelements of principal environmental concern. Data for EDTA and citrate are also included and a guidance note [20] has been prepared to assist participants in the modelling of natural organic acids. Versions of

the database have been distributed in PHREEQE [6] and/or MINEQL [7] formats to all CHEMVAL participants plus others in North America and Australia. An update will be distributed in April 1989 including a listing in EQ3/6 format [8].

A report on database activities has been produced [19] giving a comparison of databases employed at the University of Wales, PSI and AERE. Reports on the comparison of methods for activity coefficient correction and recommendations for experimental investigations are in preparation, and will be available during the Summer of 1989. At the end of the project the results of each University's work will be comprehensively reported and published, together with a final version of the CHEMVAL Database, in dBase III+ format.

The programme of work summarised above is proceeding in parallel with a number of complementary studies around the world. In order to improve co-ordination and further disseminate the results produced, representatives of the OECD/NEA are invited as observers to all CHEMVAL Plenary Meetings. Information has also been sent to CODATA and inaccuracies identified in "standard" compilations have been reported to IUPAC.

6. TASKS OUTSTANDING

Stages 2 and 3 of CHEMVAL are nearing completion and will be reported in Autumn 1989. Stage 4 constitutes a first attempt at providing some degree of validation for coupled models and has just begun. Given the data requirements of such models and the scarcity of suitably complete experimental information no more than two cases can realistically be attempted with the resources available. Efforts will be concentrated on well-defined column experiments of neptunium migration [21] and flow-through studies on Fontainebleu Sands [22]. The two case studies will be defined jointly with personnel involved in the original experiments.

Findings will be reported in December 1989, coinciding with the final issue of the CHEMVAL Thermodynamic Database. Thus, both modelling and database activities are on course for completion in January 1990.

ACKNOWLEDGEMENTS

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STAGE	RELEASE DATE	AQUEOUS SPECIES	SOLID SPECIES	FORMAT
1	JUNE 1987	376	259	PHREEQE MINEQL
2	MAY 1988	521	327	PHREEQE MINEQL
3	APRIL 1989			PHREEQE MINEQL EQ3/6
4	JANUARY 1990			DBASEIII+

Table I Status of CHEMVAL Thermodynamic Database

ELEMENT	AQUEOUS SPECIES	SOLID PHASES
Pu	Pu(OH)_5^- PuCO_3^+ PuCO_3^{2+} & $\text{Pu(CO}_3)_3^{2-}$	$\text{PuO}_2/\text{Pu(OH)}_4$
Am	$\text{Am(OH)}_2\text{CO}_3^-$ & Am(OH)_2^+ AmCIT & AmEDTA^-	AmOHCO_3
U	U(OH)_5^- $\text{UO}_2(\text{CO}_3)_2^{2-}$ $(\text{UO}_2)_3(\text{OH})_5^+$ & $(\text{UO}_2)_2(\text{OH})_3\text{CO}_3^-$ $\text{UO}_2\text{EDTA}^{2-}$ & UO_2HCIT	$\text{UO}_2/\text{UO}_2 \cdot 2\text{H}_2\text{O}/\text{Uraninite}$ $\text{UO}_3/\text{UO}_3 \cdot 2\text{H}_2\text{O}/\text{Gummite}$ $\text{CaUO}_4/\text{Na}_2\text{U}_2\text{O}_7$ $\text{U}_3\text{O}_8/\text{U}_4\text{O}_9$
Tc	Tc(IV)/Tc(VII) couple	$\text{TcO}_2(\text{am})/\text{TcO}_2(\text{c})$

Table II CHEMVAL Stage I Priority Species for Database Enhancement

PROCESSES	SYSTEM			
	MOL Am, Pu, Np	GORLEBEN Am, Pu, Np	MAXEY FLATS Am, Pu	OMAN U
AQUEOUS SPECIATION	*	*	*	*
PRECIPITATION- DISSOLUTION	*	*	*	*
pH BUFFERING	*		*	*
REDOX EQUILIBRIA	*	*	*	*
IRREVERSIBLE OXIDATION/REDUCTION	*		*	
ORGANIC COMPLEXATION	*	*	*	
pCO ₂ VARIATION				*

Table III CHEMVAL Stage 2 - Principal Features of Model Systems

PROCESSES	TEST CASE		
	1 CEMENT NEAR-FIELD	2 BENTONITE ALTERATION	3 ACTINIDE TRANSPORT
AQUEOUS SPECIATION	*	*	*
PRECIPITATION -DISSOLUTION	*		
ADVECTION	*		*
DIFFUSION		*	
ION-EXCHANGE		*	*
RADIOACTIVE DECAY			*

Table IV CHEMVAL Stage 3 - Principal Features of Coupled model Verification Exercises

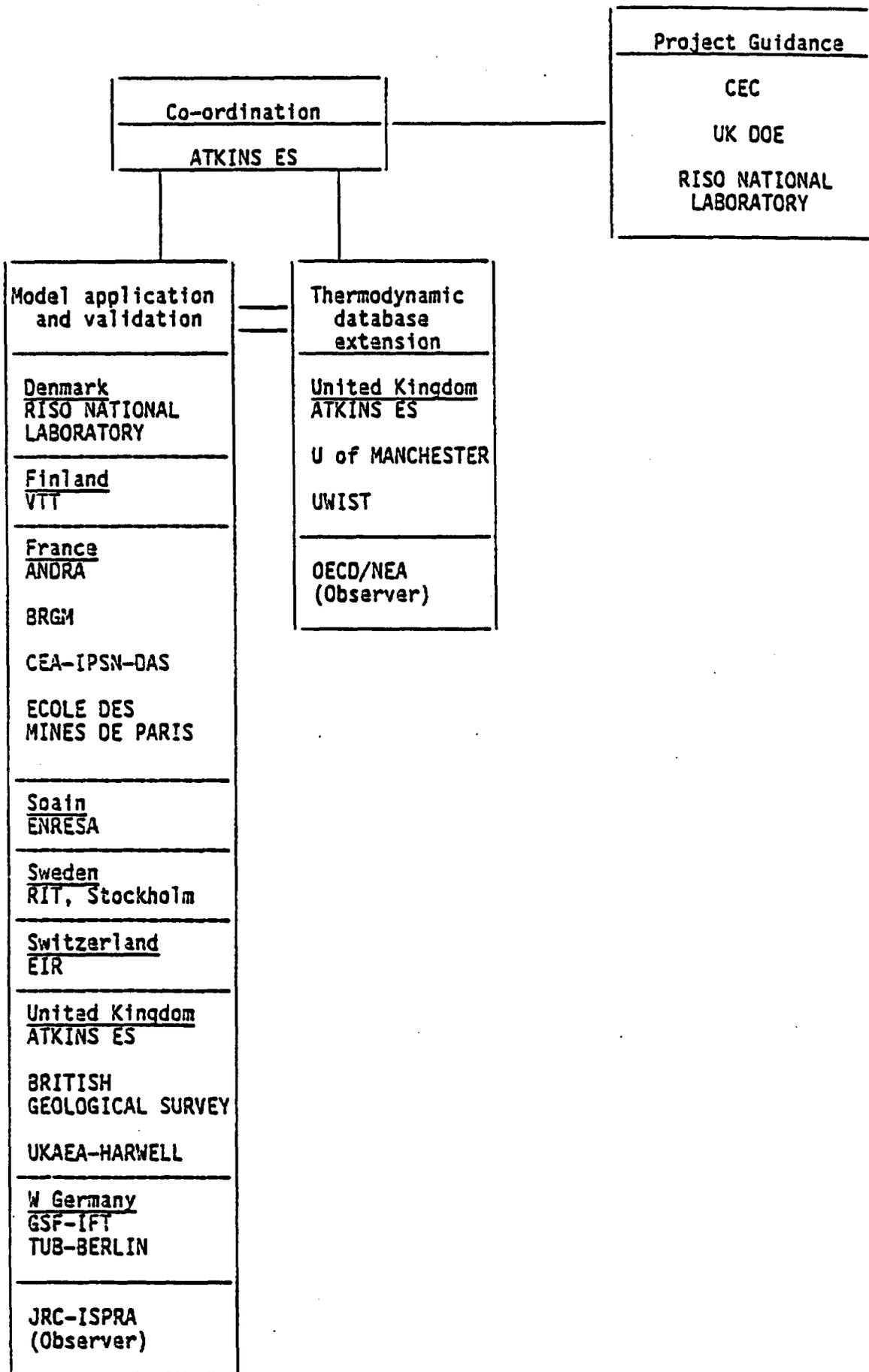


FIGURE 1 ORGANISATION OF CHEMVAL

FIGURE 2 CHEMVAL : STAGE 2
MOL:- AMERICIUM AND NEPTUNIUM SOLUBILITY
IN SYNTHETIC CLAY WATER

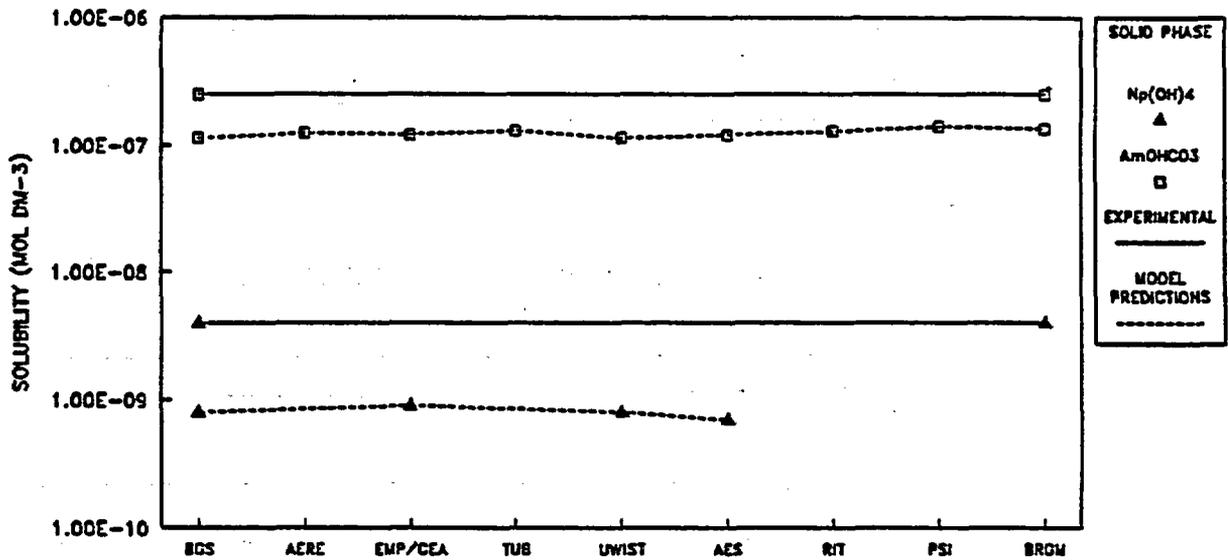
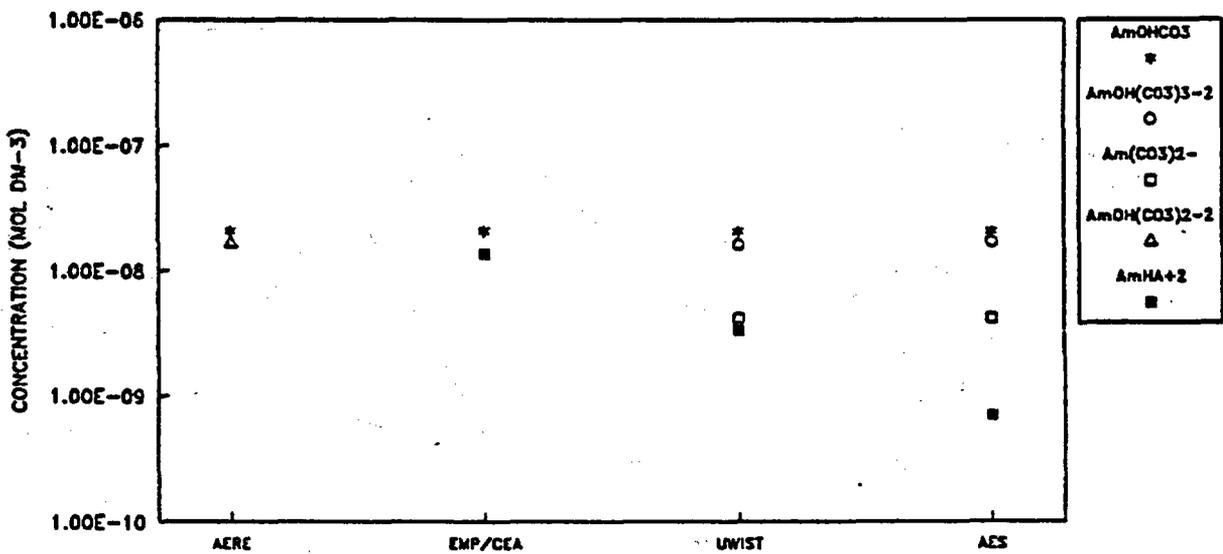
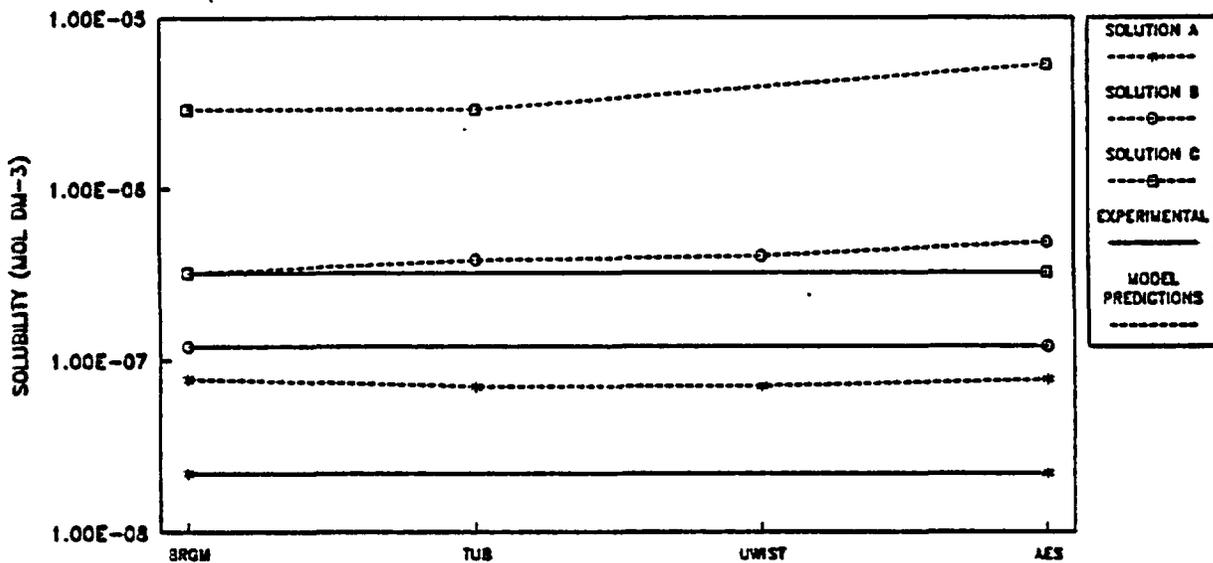


FIGURE 3 CHEMVAL : STAGE 2
MOL :- AMERICIUM SPECIATION IN
INTERSTITIAL CLAY WATER



**FIGURE 4 CHEMVAL : STAGE 2
AMERICIUM SOLUBILITY IN
GORLEBEN WATERS**



**FIGURE 5 CHEMVAL : STAGE 2
GORLEBEN :- PLUTONIUM SORPTION IN
PRESENCE OF CITRATE**

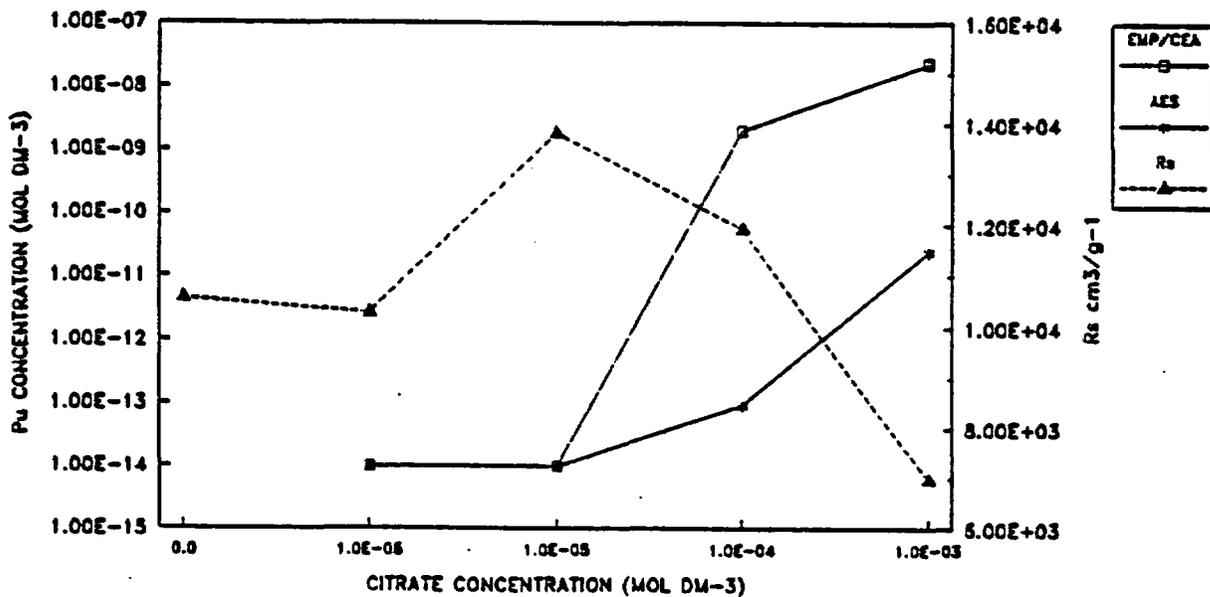


FIGURE 8 CHEMVAL : STAGE 3
TRANSPORT OF U-234
BATEMAN'S SOLUTION

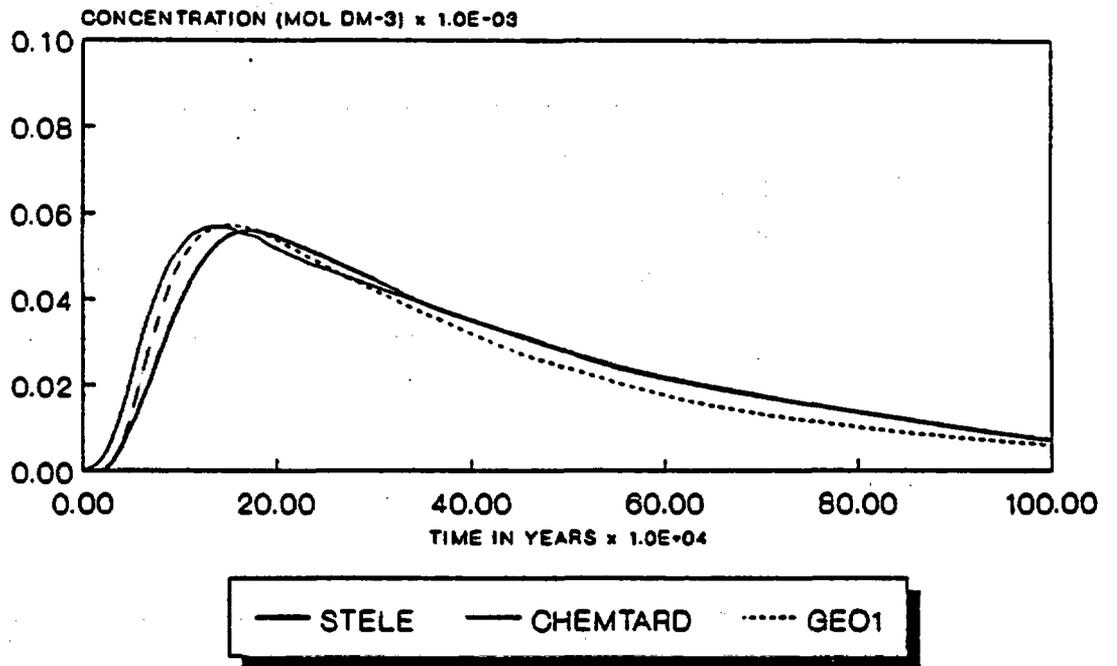


FIGURE 9 CHEMVAL : STAGE 3
CEMENT NEARFIELD
pH PROFILE AT 200 YEARS

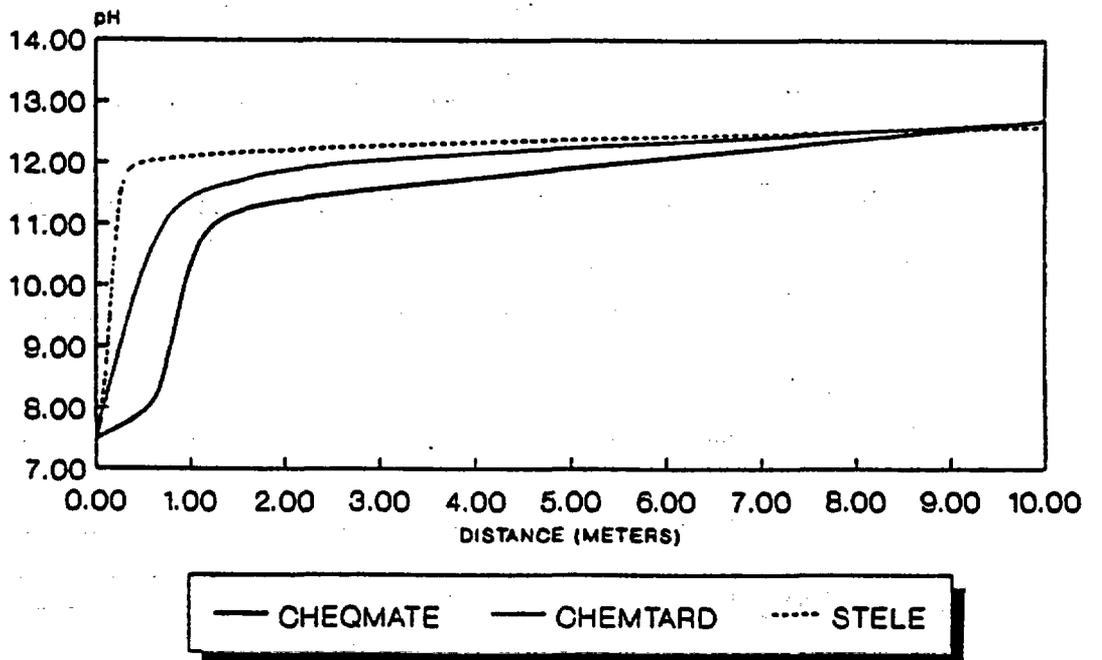


FIGURE 6 CHEMVAL : STAGE 2
GORLEBEN:- AMERICIUM SORPTION IN
PRESENCE OF EDTA

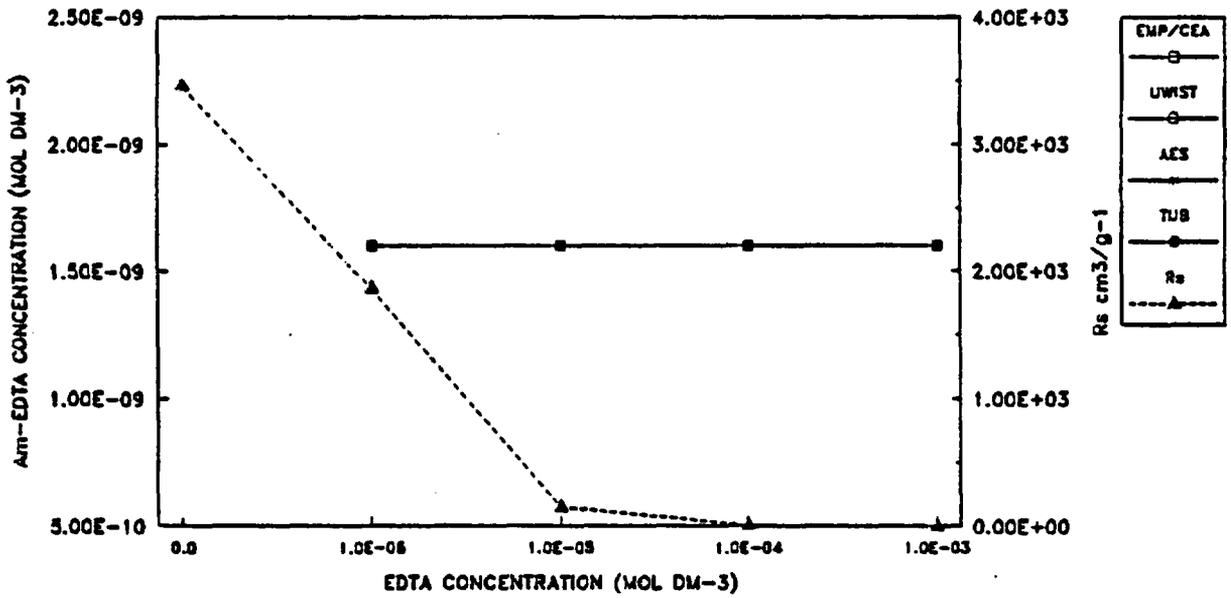
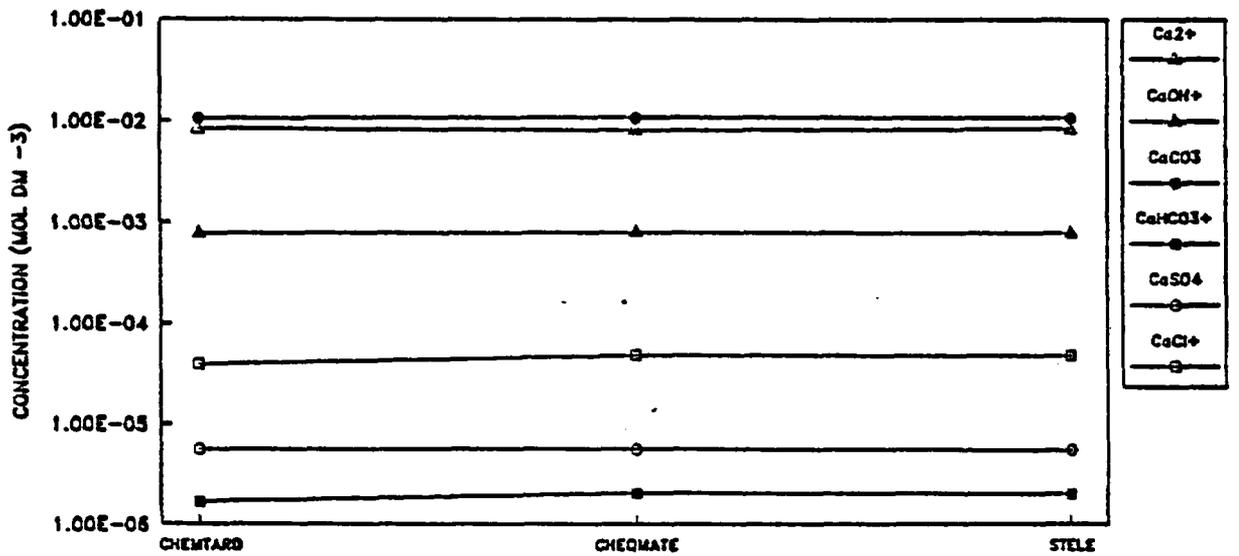


FIGURE 7 CHEMVAL : STAGE 3
CALCIUM SPECIATION IN
CEMENT LEACHATE



WORKING DOCUMENT
RESTRICTED DISTRIBUTION

ATTACHMENT 5

COMMUNITY PROJECT MIRAGE (second phase)

Plenary Meeting

Bruxelles, March 16-17, 1989

Review of work done in research area

" In-situ migration experiments and development of measuring techniques"

by

A. Avogadro

1. INTRODUCTION

The broad objective of this research area is to verify, by means of in-situ field tracer tests, predictions of the mobility of radionuclides under realistic natural conditions.

Models describing underground pollutant transport are affected by uncertainties due to incomplete knowledge of the processes involved. Although the majority of phenomena controlling the underground migration are known, the precise measurement of controlling parameters and their extrapolation to wide areas is not simple and customary. The scale of the phenomenon is in fact of great importance. From the laboratory observation of the pollutant-soil interactions (microscale) is necessary to proceed to the study of the phenomenon inside the aquifer (mesoscale), controlling the groundwater flow by abstraction and/or injection wells. All these data taken together and conveniently combined with hydrological data will provide the necessary information for the interpretation of the phenomenon in a regional scale (macroscale).

Since its inception, the MIRAGE project considered site-specific migration experiments a necessary effort for the understanding and quantitative description of the sub-soil transport.

Three different approaches have been adopted by the laboratories participating to the MIRAGE project under this item:

- a) in-situ migration experiments (BGS, Keyworth, Contract 64; SCK-CEN-Mol, Contracts 55 and 145; UKAEA-Harwell, Contract 154)
- b) laboratory experiments with simulation of natural geochemical environment (JRC-Ispra)
- c) migration experiments in real natural environments making-use of special probes placed inside a well drilled at the site under study (CEA-Cadarache, Contracts 65, 87 and 144).

All these projects have been already presented last year as new projects or extension of previous contract with the CEC. The advancement is progressing steadily even if it does not appear very rapid, as normally happens in such type of works where scientific, technical, radio-protective and licensing implications are involved.

2. WORK REVIEW

2.1 In-situ migration experiments

BRITISH GEOLOGICAL SURVEY (BGS)-Fluid Processes Research Group

The objective of this project is the study of the migration of radionuclides in a shallow glacial sand aquifer and in particular the potential effect of organics (natural or introduced) on radionuclide speciation and mobility.

The tracer tests are being undertaken in a remote part of the low level radioactive waste disposal site at Drigg in Cumbria. Prediction of their outcome is based upon detailed hydraulic characterization of the field site, coupled with laboratory studies of radionuclide sorption and organic complexation.

a) Aquifer characterization and instrumentation

Groundwater is re-circulated between two boreholes 3,41 m apart and the tracers are released in a third "on-line" borehole 0,94 m from the recharge well. Migration is monitored by means of three in-situ gamma detectors, and by removing groundwater from three multi-level sampler installations (figure 1). Flow lines are assumed to be parallel in the vicinity of tracer release and monitoring wells such that a 1-D advection-dispersion model can be used at least for preliminary dispersivity assessment.

During array construction, profiles of hydraulic conductivity were determined at 75 mm intervals at 3 locations, giving a range of values between 1×10^{-6} and 1×10^{-5} m/s. A pumping test gave K as 10^{-6} m/s. Porosity (approx. 0.35) has been determined from core material. The test has been modelled assuming a homogeneous single layered aquifer 1 m thick and porosity 0.35. Predicted travel times at a re-circulation rate of 2 l/min vary between 9 and 29 hours from nearest multilevel sampler to recovery (i.e. pumping) well.

Two tracer tests have been conducted at re-circulation rates of 2 l/min. An initial test with inactive chloride was compared with a test using Iodine-131 and Tritiated water. Results show that iodide and chloride move at approximately the same rate but tritium is slightly retarded. Dispersivities were determined using a curve fitting technique based on the 1-D advection-dispersion equation with an exponentially decaying source. Longitudinal dispersivities were generally 2 orders of magnitude smaller than the migration distance, at around 4.5×10^{-3} to $1,3 \times 10^{-2}$ m. The fastest time to peak breakthrough was 3,25 hours, 3 times faster than predicted. This is due to heterogeneities in the aquifer which necessitates a more complex model. A layered system has therefore been considered in which layers are assumed to be 15 cm thick (equivalent to the vertical separation between multi-level sample points). The influence of the boreholes, gamma probe access tubes and multilevel samplers has not been considered; it is suspected that little effect would be identified compared with the effect of aquifer heterogeneity.

Apart from hydraulic properties of the aquifer, its geochemistry and mineralogy characterization is being carried out. A large volume of water (325 litres) removed from the array has yielded 60 mg Humic Acid (HA) and 800 mg of Fulvic Acid (FA) whose properties are studied in the framework of the COCO Club and

reported in the research Area "Geochemistry of Actinides and Fission Products".

AERE-Harwell sampled Drigg groundwater for colloids using dia-ultrafiltration and characterized in term of their physical and chemical properties. As a matter of fact, in order to investigate possible migration of Radionuclides through colloid transport, it is necessary to fully characterize the natural colloids in the aquifer. Once this is done it should be possible to carry out colloid mobility measurement in both field and laboratory experiments. Measurements on groundwater from the Drigg aquifer suggest that there are iron organic complexes at a concentration of about 10^9 particles/litre in the size range 0.05-1 micron, having associated with them up to 7% of total Th-230 and less than 1% of total Uranium present.

b) Laboratory studies

Column experiments were used to simulate the migration of various organic-radionuclide complexes in the field tracer test and to identify the dominant sorption mechanism. In particular the columns provide data on the stability of the Cobalt-FA complex in order to demonstrate the feasibility of utilizing Cobalt in a field tracer test, as well as to validate R_d values estimated from previous batch sorption experiments. Cobalt complexed with natural organic material (Fulvic Acid) extracted from Drigg aquifer was used in column experiments. Assuming that only uncomplexed Cobalt as Co(II) ion is sorbed by the soil, and that the rate at which the Cobalt-groundwater complex dissociates control the rate of production of uncomplexed Co, the sorbed Cobalt concentration gradient along the column should be a simple function of the dissociation constant of the groundwater complex and the solute transport velocity.

The kinetics of dissociation were determined by sectioning the column and establishing the distribution profile of the Cobalt. A rate of $1,81 \times 10^{-5} \text{sec}^{-1}$ was inferred for the dissociation reaction.

The Co-FA complex would therefore not be expected to migrate significantly within the field experiment period. The choice of radionuclide-organic species for future tests has not been decided; the results of sorption work with Eu, Np and U show that these elements are still strongly sorbed under most conditions studied, and suitable short lived isotopes are not available. Cerium-141 which is an analog for tri- and tetra-valent actinides may however be useful.

c) Modelling

Geochemical modelling of Drigg groundwater and of the solute migration in the tracer tests has been undertaken jointly by University of Wales Institute for Science and Technology and BGS. The activity in this field is reported in the Research Area "Calculation Tools" of this meeting.

SCK-CEN-Mol (Belgium)

Experiments related to in-situ migration of radionuclides are being performed in the Boom Clay surrounding the Underground Research Laboratory (URL) at SCK-CEN site of Mol (Contracts No.55 and 145). This research is carried out with the aim to verify the diffusion parameters as determined in the surface laboratory,

to validate the migration models and to gain public acceptance.

The migration of radionuclides in the argillaceous medium is described by a transport equation which incorporates the following main parameters:

- the product of the effective porosity η (i.e. accessible for the diffusing species) and the Retardation Factor R;
- the apparent dispersion constant D of the solutes;
- the Darcy velocity Vd, i.e. the product of the hydraulic conductivity and the hydraulic gradient.

The first two parameters are measured in laboratory and are verified by in-situ experiments. The hydraulic conductivity and pressure gradient are determined by means of piezometers installed in the clay formation. The flow rate is determined by weighing the water collected over periods from several days to several weeks depending upon the filter size of the piezometers; the pressure of the pore water percolating through the filter is measured by Bourdon manometers. The value of the hydraulic conductivity at the different piezometer locations vary between $3,1 \times 10^{-12}$ m/sec to $3,6 \times 10^{-12}$ m/sec and is independent from the depth (no overburden correlation).

These measurements demonstrate the good homogeneity of the formation, as filtering surfaces from 1cm^2 to 1m^2 placed over half the thickness of the clay layer gave very low variability in the hydraulic conductivity. The values of the pore pressure gave a regular variation as a function of the distance from the gallery, suggesting that the pressure profile is determined by the experimental drift (Fig.2). Taking advantage of this pressure gradient, two types of underground migration experiments have been designed: a) percolation experiments with labelled clay cores emplaced in boreholes and b) direct injection of tracers in the clay formation.

a) Labelled clay cores emplaced in boreholes

A water soluble form of the radionuclide to be studied is sandwiched between two clay cores mounted into a stainless steel holder which is emplaced in a freshly drilled borehole. The narrow gap between core-holder and borehole wall is readily closed by the natural convergence of the clay. Progressively the pore water pressure builds-up and the water from the formation percolates through the labelled clay core which is supposed to be consolidated in-situ.

Table I gives the characteristics of 5 migration experiments carried-out up to now. The experiments with Europium and Strontium are completed, those with Cesium and Uranium are still underway. The flow-rate for these experiments is approximately $8 \mu\text{l/day/cm}^2$. This flow-rate exceeds the expected flow-rate in the formation by more than four orders of magnitude, due to the difference in the hydraulic gradients being 0.02 in natural conditions compared to 1400 in a clay core emplaced at 6 m distance from the underground laboratory.

Figure 3 gives the radioactivity distribution of Europium in the clay core 489 days after its emplacement in the borehole. The high concentration at the source position suggests that Europium may be considered as a constant concentration source. The tailing at the right hand of the curve indicates that a small fraction of the tracer migrates with low retardation ($K_d = 0,3 \text{ ml/g}$). The total percolated

quantity $Q(t)$ shown in Figure 4 has been fitted with the solution for the transport equation for the constant concentration source. Calculation, described more exhaustively under Research Area "Calculation Tools", gives $\eta R=0.88$ and $C_0=11,6$ cps/ml. Remarkable is the extremely low quantity leached out of the clay plug having in mind the very high Darcy velocity which is 12000 times the natural value in the formation. The Europium experiments show thence that a very small fraction of the tracer is almost not retarded while the bulk of the activity remained at the place of labelling. The role of small organic complexing substances in this mechanism is being studied, also in collaboration with the Catholic University of Leuven, and results reported under the Research Area "Geochemistry of Actinides and Fission Products".

Figure 5 gives the Strontium distribution in the clay core after 260 days of water percolation. The distribution shows that in this case the Strontium may be considered as an impulse source. The experimental results have than been fitted with the equation for an impulse source.

Calculation gives an apparent dispersion constant D of $6,9 \times 10^{-8}$ $\text{cm}^2\text{-sec}$, an apparent convection rate $V=3,7 \times 10^{-10}$ and a value for ηR of 238. The results of calculation are reported in the figure. The total quantity of Sr-85 transported through the clay plug as a function of time is shown in Figure 6. From an injected quantity of 37750 cps a small amount (5,3 cps) is transported through the clay during an accelerated water percolation of 260 days. The almost symmetrical profile suggests that the transport is in first instance due to molecular diffusion.

One year after emplacement of the experiment labelled with Cesium, no radioactivity has been detected in the pore water percolating through the clay core at a constant flow rate of 144 $\mu\text{l-day}$. The purpose is to continue this experiment until a radioactivity profile is measured in the pore water, even if waiting time of several years are required. The preservation of real pore water composition over such long periods, difficult to maintain in the laboratory, constitutes a definite advantage of this type of in-situ experiments.

b) Tracer injection with piezometer nest

The injection system, schematized in Figure 7, consists of a series of independent porous filters connected to separate outlet ports; one of these ports is used for tracer injection. It is expected that tracer injected under such conditions will migrate with almost spherical symmetry. At first, experiments will be limited to non retarded tracers. From 20.01.1988 to 10.03.1988, a stainless steel tube containing one Gigabecquerel of HTO has been connected to the injection port; a pressure difference of 3,3 bars forces the tritiated water in the clay. The purpose of this experiment is to monitor the migrating tritium by periodic sampling at the neighboring filter ports. Aside from the advantage of working on a representative scale, some drawbacks are associated with this configuration such as preferential pathways and

dead-volumes of the filters and tubings; a mini-piezometer nest has then been developed and installed on May 1988. The distance between five filter elements is 20 cm, the dead volume has been reduced and for the addition of the tracer one filter element has an in- and outlet tubing making possible the injection at the same pressure of the clay pore water. When the system is sufficiently stabilized, tracer experiments with radioactive Iodine will be carried-out.

Migration experiments with labelled clay cores and with piezometer nests are also devised in a gamma and temperature fields simulating repository conditions. To this aim a Cobalt-60 source of 15 kilocuries, surrounded with heating elements, which is being inserted in the clay formation will provide the required conditions.

In-situ tests are complemented by laboratory migration studies, which are at present non funded by CEC, in order to better define the influence of various parameters. The influence of the consolidation pressure on the diffusion parameters has been examined for several species, in particular for small organic molecules like sucrose, lactose, phenylalanine etc. These molecules in fact have been used as substitutes for small humic species. The diffusion conductivity η_{RD} is given vs the consolidation pressure in Figure 8. The regular decrease in η_{RD} with P suggests that these small, essentially non-sorbed molecules ($R = 1$), are slowed down by simple mechanical reasons related to the decrease in pore

volume. At 4.41 MPa, the consolidation pressure of the formation, a value $\eta_{RD} = 5 \times 10^{-8} \text{ cm}^2/\text{sec}$ for small humic vectors of the activity seems an appropriate choice for transport modelling. The differences in diffusion coefficient and porosity observed in relation with the method of preparation of the plug are not much more than the experimental dispersion noticed for plugs prepared by the same method. In consequence it can be stated that the method of sampling the clay in the formation and preparing it as a plug for diffusion tests, introduces only minor variation in the so-called "structure" of the clay (assuming of course that anaerobic conditions were preserved all-through the operation and that the reconsolidation has been properly carried out). Laboratory diffusion tests constitute therefore a recommendable method to investigate the migration of radionuclides in clay and can be trusted to either provide correct evaluations of transport parameters or to reveal complications in the transport mechanism.

UKAEA-Harwell : Chemistry Division

Measurements on radionuclide diffusion in clay are also planned at Harwell Research Establishment (contract 154). Laboratory work on reconsolidated plastic clay (London clay) to measure diffusivity, permeability, porosity and sorptivity gave unexpected discrepancies, making the extrapolation to natural conditions very arbitrary. For instance the porosity was found not wholly accessible by diffusion and possibly dependent upon reconsolidation procedures. Sorptivity from slurries appeared much larger than from through-diffusion experiments on reconsolidated clay (from 200 to 3000 times for Cs sorption).

As a consequence of these observations it has been decided to perform field tests to attain reliable values. The in-situ measurements are planned at the URL of Mol and sample of the Boom Clay has been brought to Harwell for laboratory comparative tests using standard methods. An existing 80 cm diameter 6,5 m long horizontal borehole lined with steel pipe will be used at Mol. The in-situ test will involve the injection of a small volume of a non-sorbed gamma-emitting tracer ($I-131$) into the clay. The diffusion of the Iodine away from the point of injection will be monitored using a collimated gamma spectrometer. As the radionuclide diffuses away from the injection point, a small component enters the collimated

beam of the spectrometer. The effective diffusion coefficient of the clay can be determined by monitoring the count-rate as a function of time. The count rate passes through a maximum thence, from a knowledge of the migration distance from the source and the time at which the maximum count rate is measured, it is possible to determine the Effective Diffusion Coefficient. A stainless steel end plate for such a tunnel was designed and manufactured at Harwell and successfully positioned against the clay face. The end plate incorporates a hole through which the injection of I-131 can be made, and a cross-like region in which the 4 cm thick steel has been reduced to a thickness of 1-2 mm. This cross produces a region where attenuation of radiation is minimal and through which measurement of I-131 migration can be made using a gamma ray spectrometer mounted on a two-axis stage. The installation of all components required for the in situ migration experiment is now complete. The movement of the collimator on the two-axis stage and the operation of the gamma ray spectrometer are controlled using a fully automated computerised system. Laboratory experiments have been performed to test the apparatus and to measure migration of I-131 in a block of Boom Clay taken from the URL.

Figure 9 shows the diffusion of I-131 away from the point of injection as a function of time. The injection point on the traverse is at the position -4 mm. The variation of count rate with time at position $X = -8$ mm is shown in Figure 10. An Effective Diffusion Coefficient of $3,5 \times 10^{-10} \text{ m}^2/\text{sec}$ is calculated. The effective diffusion coefficient calculated from this experiment is in good agreement with laboratory data published by SCK - CEN Mol, where values of between $1,4$ and $4 \times 10^{-10} \text{ m}^2/\text{sec}$ are quoted. Not all the clay formation are rather homogeneous, some have silty or sandy layers and, if hard enough, also fractures. These fractures may provide paths for flow and solute connection much faster than convection and diffusion through the bulk of the clay.

The investigation on the rate, retardation and dispersion of radionuclide leakage through such paths can only be carried out through field work. A second project is therefore planned on fast leakage paths and will be done in the Kimmeridge Clay lying 10 to 40 meters below the UKAEA site of Culham, Oxon. This clay formation has been chosen because it appears to contain the geological fractures of interest at easily accessible depth and because it is conveniently close to Harwell.

For the main objective, cores will be obtained from holes drilled through the 30 m of clay. Some of these cores will be split axially and logged for any silts, sand and observable natural fractures. On the basis of this, samples will be sub-cored for laboratory measurements. This information will be used to isolate and pressurize for flow measurement lengths of holes at these depths. If the properties of the clay allow, movable packers will be used; if not, new holes may have to be drilled to the appropriate depth for pumping flow through stand pipes to the required positions.

Comparison of flows into silts, sand and fractures and into the clay will then show how greatly the former features influence flow and convection and the extent to which they should be explicitly taken into account in modelling of radionuclide leakage. Planning permission for field work at Culham was granted in June 88 by the South Oxfordshire District Council. No progress has been made with the work at this date. Field investigations will begin at the Culham site early in 1989.

2.2 Laboratory simulation experiments (JRC-ISPRA)

Site specific materials representative of geologic systems surrounding potential nuclear waste repositories are used for laboratory migration experiments. Porous material from the clayey aquifer of Mol containing about 25% of Glauconite, and quartz sand with small amount of pyrite and magnetite, taken over the salt dome of Gorleben were chosen. A constant water flow-rate through glass columns filled with the soil is maintained; the column dimensions are 200 mm in length and 25 mm in diameter. The inflow solution is contaminated by leaching of doped borosilicate glass beads. The glass is separately traced with 0,58 wt% of Tc-99, 2 wt% of Np-237 and 0,05 wt% of Pu-238. Flow-leach experiments are carried out under oxic and anoxic conditions. Experiments under anoxic conditions involve the use of anaerobic chambers containing nitrogen atmosphere. A controlled partial pressure of Carbon Dioxide (0,1%) and a small fraction of Hydrogen is set-up for percolation experiments under anoxic conditions. Constant Eh values ≤ -200 mV (platinum electrode) is maintained. Two different leaching solutions, either a synthetic bicarbonate groundwater simulating that present in the aquifer overlying the Boom clay or saturated NaCl brine typical of the saline area surrounding the Gorleben salt dome were tested. The average leach-rates are reported in Table II.

First migration tests conducted with Tc-99 and Mol groundwater under normal oxygen atmosphere showed a few percent of leached Technetium retained by Glauconitic sand, supporting the presence of the non-sorbing anionic form (pertechnetate) under oxic conditions. A higher retention (72%) of Tc-99 was measured in the absence of oxygen. This behaviour is typical of cationic species of Tc(IV). The migration behaviour of Neptunium, another redox sensitive radionuclide, was also investigated both in the Mol groundwater and in NaCl saturated brine. Ultrafiltration analyses of the leachates under oxic conditions showed the absence of colloids of Neptunium which appeared to be released from the glass as soluble species of Np(V). Nevertheless, similar results were also found (both Mol groundwater and saturated brine) under the anoxic conditions investigated, where the stronger colloid-forming tetravalent Neptunium should prevail. Retardation factors were then measured for the columns loaded with these Np(V) containing leachates in normal oxic conditions and in the anoxic atmosphere boxes. Results are given in Table III. Similar to Tc, the exclusion of oxygen decreased the mobility of Np. However, important differences were observed between the synthetic bicarbonate- groundwater-Glauconitic-sand system and the Gorleben-groundwater-quartz-sand system. In the first, all the applied Np was recovered from the soil, whereas in the second, a constant column breakthrough (about 20% of the input activity) was detected continuously during the percolation. The lower Np recovery in the latter may be attributed to the lower proportion of weathered clay minerals, which are known to bind actinides strongly.

However, a decreasing Np gradient measured through the column in the quartz sand system indicates that saturation of the sorption capacity was not reached. Under these conditions, the concentration of mobile Np might correspond to a species not in local equilibrium with the soil. Under brine solution condition, competition for surface sites, or the presence of chloride ions, which can form soluble not-retained complexes with Np may be responsible for the decrease of sorption. In the case of Plutonium, irrespective of the soil-water system, higher

retardation factors values were measured under anoxic conditions. No significant difference was found in Pu retardation due to the higher ionic strength of the brine solution. Results are also given in Table III.

Migration experiments were also carried-out in order to study the influence of natural organic ligands on Plutonium retention. A column was packed with the Mol sand and then equilibrated with a continuous flow of organic-free groundwater under reducing conditions. Breakthrough curve of non-sorbing solutes was determined by tritiated water percolation.

The Humic Acid (HA) extracted from Boom Clay was then added to the groundwater to a concentration of 25 ppm and the solution was passed through the column. The behaviour encountered for HTO and HA is illustrated in figure 11. It can be seen that HA transport differs appreciably from that of a conservative tracer. The HA breakthrough curve is shifted to the right showing a much broader transition zone. Moreover, a steady-state condition of unchanging effluent concentration at value below that of influent ($C/C_0 = 0.8$) was reached. This non-equilibrium situation was followed for percolation times longer than those reported in figure. Ultrafiltration of the column effluent showed that HA colloids smaller than 400 nm were eluted ahead of larger particles.

The interception and accumulation on the grain surface of relatively large particles compared to the grain size led to their removal from the suspending fluid. For small enough HA particles, penetration into small pores, where the velocity of water is low, can result in mechanical straining. Due to the polydispersed nature of the HA suspension in the groundwater flow, the net effect of this straining mechanism would be to widen the transition zone of the breakthrough curve. The chemical association of Pu with moving HA was investigated by leaching of ²³⁸Pu-doped borosilicate glass. Figure 12 shows an enhancement of Pu release rate when HA is added to the flowing groundwater under reducing conditions. Attack and dissolution of cations in the glass structure decrease the glass durability enhancing Pu release; the role of HA on life-span of nuclear waste deserves hence further examination. Under static conditions, about 30% of total Pu was found to be associated with HA particles; however, no breakthrough was monitored in the column experiment (Pu inlet concentration about 10^{-10} M) even after percolation of 20 bed volumes of Pu-contaminated leachate. A comparison with the HA breakthrough curve shows that Pu movement is further delayed. This indicates that adsorption sites on the sand successfully compete with binding sites of moving HA particles to remove Pu from the water flow. In flowing systems therefore, Pu binding to small HA particles, moving through voids between mineral grains, does not appear to hinder Pu adsorption on the Glauconitic sand. To gain insight into Pu transport mechanism, studies to determine rate and extent of Pu binding by HA particles are in progress.

A separate project carried out in collaboration with Hahn Meitner Institut-Berlin, concerns the retention properties of the crushed rock salt used as backfill material of a repository in a salt dome. After the possible leaching from the waste-form, the backfill material will be the first barrier for the radionuclide migration. Cavities backfilled with crushed rock salt will have an initial porosity of about 30% which will decrease with time due to the creep behaviour of the salt. Salt columns of different porosity (from 4 to 12%), prepared by BGR-Hannover (FRG) by isostatic pressing of ground salt were installed in a alpha glove-box at normal oxic

condition, and a leachate of controlled concentration was percolated through the columns making use of a peristaltic pump. First measurements of the retardation properties of pressed rock-salt yield an effective retardation of Am and Pu but almost no retention of the more relevant elements Np and Tc. For Pu only the column with the highest porosity (residence time of the order of one day) exhibited a non instantaneous breakthrough curve; a maximum retardation factor of 12 was estimated. For Americium an apparently high retardation factor of 100 has been observed; the concentration profile along the column axis is overlaid by intensive peaks indicating non homogeneous adsorption. A possible explanation might be the occurrence of colloidal particles in the leachate. For Np and Tc a possible influence of the redox potential should be investigated.

2.3 Geochemical probes (CEA;CEN-Cadarache)

To avoid possible uncertainties connected with laboratory simulation experiments, these probes allow to study sorption-desorption phenomena in real geological conditions. They are in fact placed inside the boreholes where the column material comes in equilibrium with the real in-situ geochemical environment. Three different probes are under development at the CEN-Cadarache: Foralab, Autolab and Chromato.

Foralab probe (Figure 13)

This probe allows to measure the Retardation Factors of radionuclides in deep geological environments (Contract No.65). The operating principle is as follows: the probe, which contains a column filled with the material under study, is placed inside the well. A pump circulates the water drawn at the selected experimental level through the column. At the base of the column, a remote-controlled syringe allows the nuclide to be introduced and a fraction collector at the top of the column allows the outlet to be sampled thus making possible to subsequently determine the breakthrough curve in laboratory. The probe is conceived as an autonomous laboratory and does not contaminate the environment since it does not discharge effluents. Only in the initial equilibration phase, before introducing the tracer, does the groundwater pass through the system and become discharged outside. The column consists of a steel tube (200 mm length) having a 20 mm inside diameter. The fraction collector includes 40 containers of 10 cm separated by 40 microvalves operated by an external computer. The mechanical and electrical behaviour of the prototype has been tested in the laboratory and subsequently on the site of Auriat at 40 meters depth. These qualification tests on a sand column involve performing the following functions which are controlled from the surface by computer: equilibration-injection of 2 ml of brine solution-drawing of 36 samples sequence. During the long testing period, some problems arose due in particular to temperature rising at the electrovalve seatings. This drawback has been recently solved by changing the power supply system and adding a finned radiator.

Autolab probe (Figure 14)

This second probe for the in-situ measurement of the diffusion of radionuclides in porous media is simpler, since it has no moving gears as the previous convecting system requires. The Autolab probe consists of a 5 litres volume reaction room (65 mm diam., 1500 mm high), which can contain up to 10 columns of porous material. The operating principle is the following: the probe is placed

inside the well and the porous material is equilibrated with the water at the selected experimental level. The reaction room is equipped with openings towards the outside which can be open or closed utilizing the hydrostatic pressure inside the well. To this end is sufficient to lower the probe to activate an hydraulic valve which is normally kept closed by a calibrated spring. When the valve is open hydrostatic pressure acts on a piston which opens or closes the openings towards the outside. In the "on" position the geological material is at first allowed to equilibrate with the ground water; then, after having closed the openings, the radionuclides are released by remote control by crumbling of a glass bulb containing them. A small battery-operated stirrer promotes homogenization. A double tracer diffusion system (Tritium-lanthanide or Tritium-actinide) will be used and the apparent diffusion coefficient will be measured in the laboratory by destructive analysis of the column. The probe has been firstly tested on the granitic site of Auriat using Europium over a 4 months diffusion time. In-situ long term measurements can possibly be performed at the Mol or Gorleben sites.

Chromato probe (Figure 15)

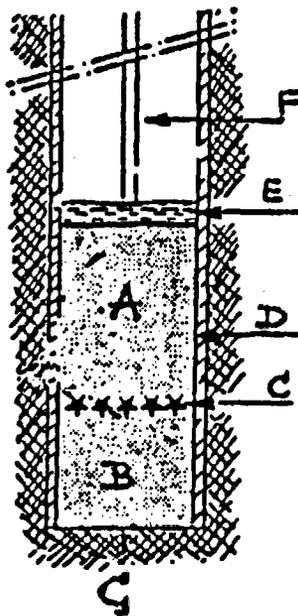
The development of this probe actually falls within another section of the CEC Programme on Radioactive Waste. However, given its close connection to the above topics, this item will also be reported here for sake of completeness. This is a more complex geochemical probe to be used in boreholes in order to analyse the water concentration of natural microcomponents which compete with actinide sorption. The Lantanides for instance, as analogues of actinides, have a strong influence on sorption processes. The task of this probe is to collect a representative sample of deep waters under equilibrium conditions and to concentrate the lanthanide fraction making-use of chromatographic columns. These columns will be further-on analyzed in the laboratory.

The probe under development is composed of six modules: after being filtered the groundwater is mixed with nitric acid to reach a pH of 1,8. At this pH value the fixation of alkaly metal ions, which represent the macrocomponents in solution, is avoided. The lanthanides are therefore concentrated in columns of Nucleosil S.A. (a porous silica material with grafted sulfonated functions). Eight columns can independently be connected along the fluid pathway, allowing the measurement at 8 different groundwater depths. The lanthanide content in the columns is then analysed in laboratory by gradient elution chromatography. The two remaining modules consist of the waste reservoir section and electronic control of the probe. The hydraulic and electric design of the probe has been tested in laboratory; Taking advantage of the "Foralab" experience, modifications have been brought on electronic control and on electrovalve seatings, in order to avoid temperature rising.

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Borehole			Clay cores and tracers					Emplacement	retrieval	
access hole	d	l	A	B	φ filter paper C	radio-isotope	activity Bq	date	technique	date
55	85	3520	45	24	31	152+154 Eu	1.78 E+6	15.10.85	underboring	07.12.87
43	50	3000	40	30	31	152+154 Eu	1.78 E+6	16.10.85	underboring	17.02.87
44	50	3000	44	28	28	Cr-85	3.7 E+6	12.08.87	underboring	27.11.87
53	50	8400	45	25	28	Cs-134	3.0 E+6	03.07.87	overcoring	
62	50	6400	31	40	28	U-233	3.50 E+4	24.11.87	overcoring	



A and B = clay cores ϕ 32 mm

C = filter paper labelled with tracer

D = SS-housing (SS = stainless steel)

E = sintered SS-filter

F = SS-outlet tube : ϕ 4-2 (outer and inner diameter- for Eu-experiment
 ϕ 1-0.6 for Sr-, Cs- and U-experiment

G = direct contact with clay formation, except borehole 55 where core B is
on top of a 50 cm high sand column

d and l = diameter and length in mm.

Table I : Characteristics underground migration experiments with labelled clay cores eaplaced in boreholes

Table II - Summary of release rate ($\text{g} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$) from borosilicate glass under flow conditions (1.5 ml/h) at 25°C.

	Bicarbonate groundwater		Salt brine	
	Oxidizing	Reducing	Oxidizing	Reducing
Tc-99	$9.5 \cdot 10^{-8}$	$1.8 \cdot 10^{-8}$	-	-
Np-237	$1 \cdot 10^{-6}$	$6 \cdot 10^{-8}$	$1 \cdot 10^{-6}$	10^{-7}
Pu-238	$4 \cdot 10^{-7}$	$9 \cdot 10^{-8}$	$3 \cdot 10^{-7}$	10^{-7}

Table III - Measured retardation factors.

System	Conditions	Pu	Np	Tc ^{a)}
Synthetic bicarbonate water/ glaucinite sand	Oxic	10^4	$2 \cdot 10^3$	3.9
	Anoxic	$6 \cdot 10^4$	$5 \cdot 10^3$	72
NaCl brine/quartz sand	Oxic	$9 \cdot 10^3$	39	-
	Anoxic	$4 \cdot 10^4$	162	-

a) % activity sorbed.

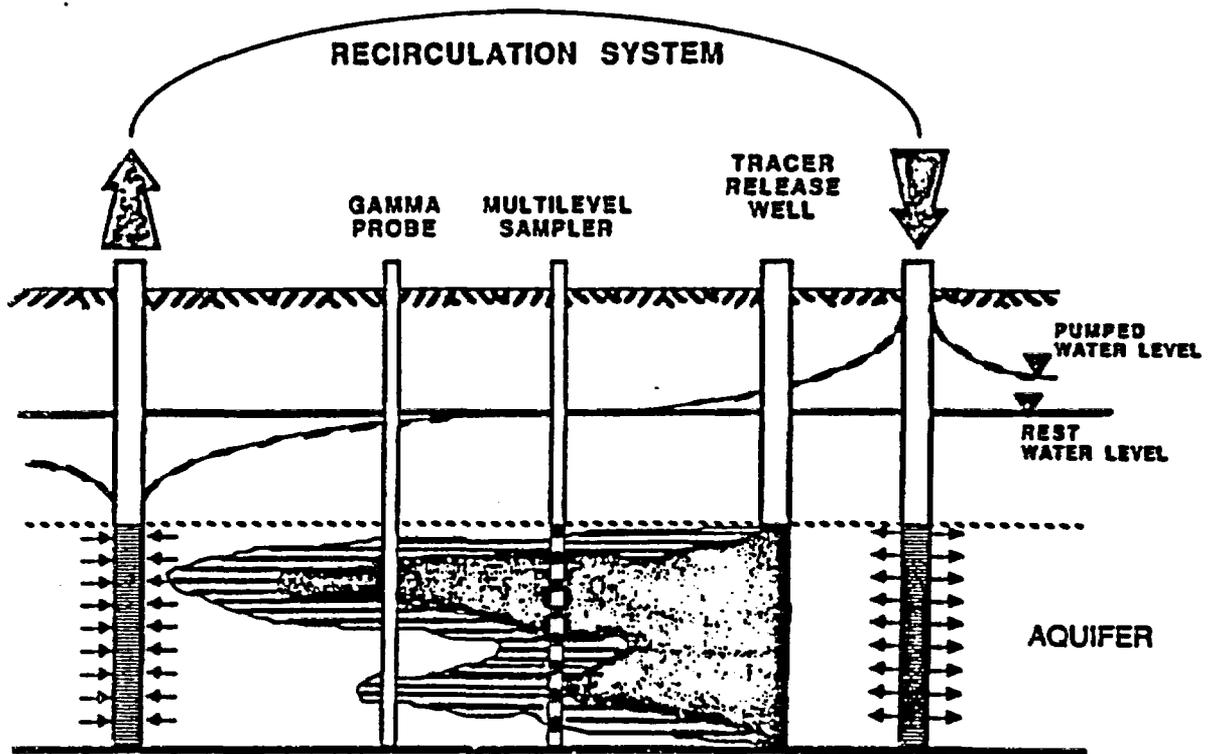


Figure 4. Diagram of the tracer test arrangement at DRIGG (BGS, 1988)

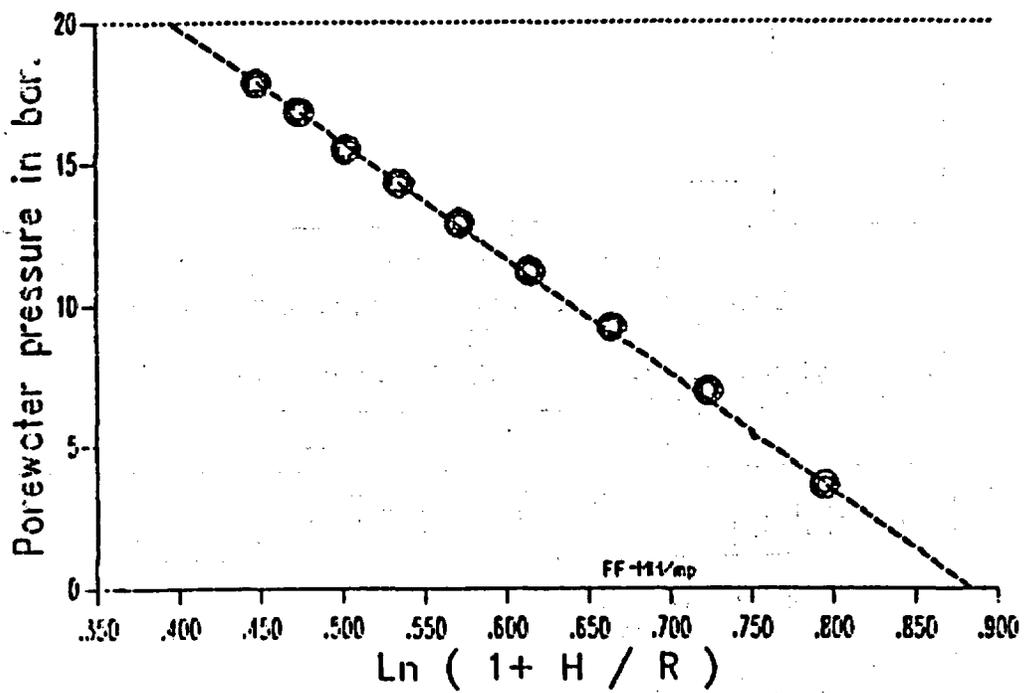


Figure 2. Pressure profile in piezonest CPI
(CEN/SCK, 1988)

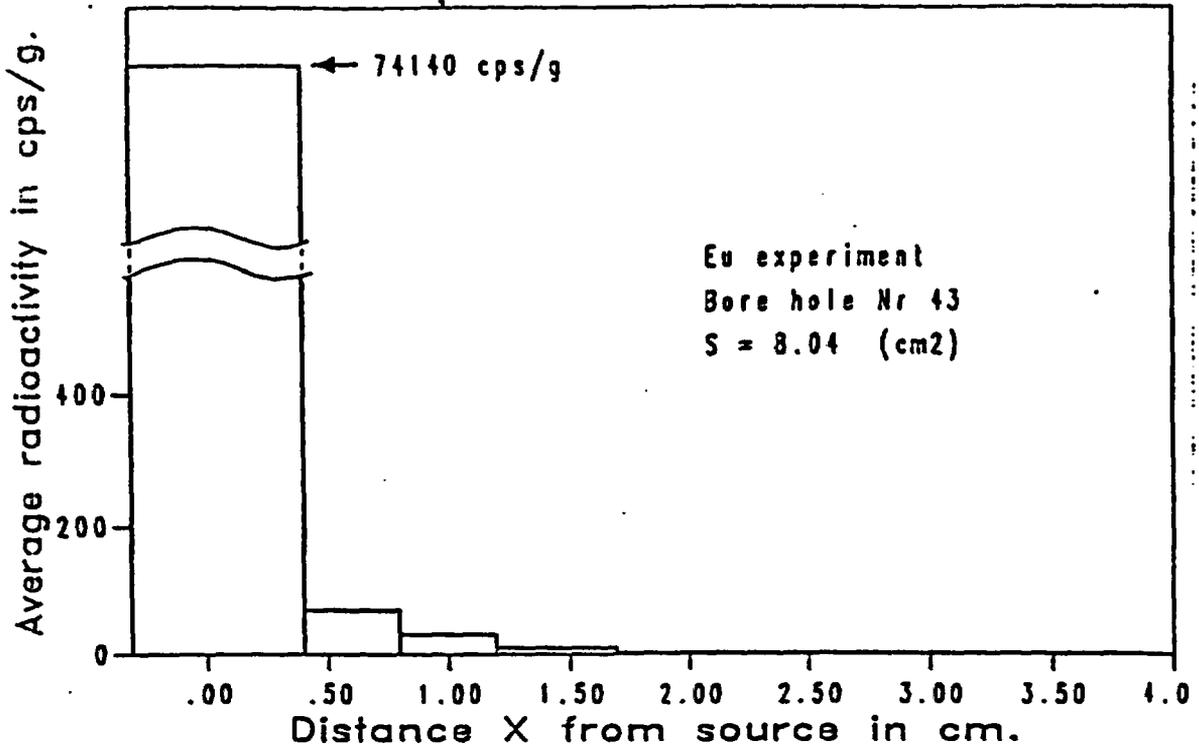


Figure 3. Europium radioactive profile in the clay plug of borehole 43 after 489 days of water percolation

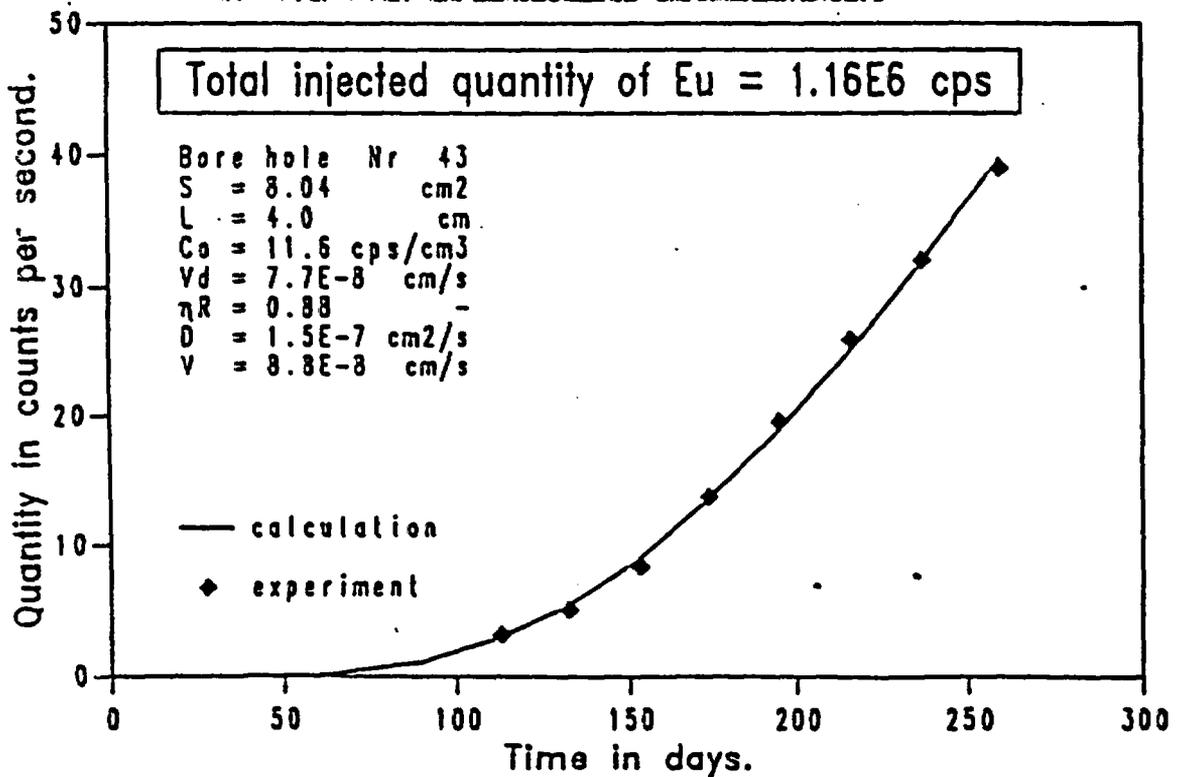


Figure 4. Total quantity of Europium transported through the clay plug of borehole 43 by the combined effect of advection and diffusion

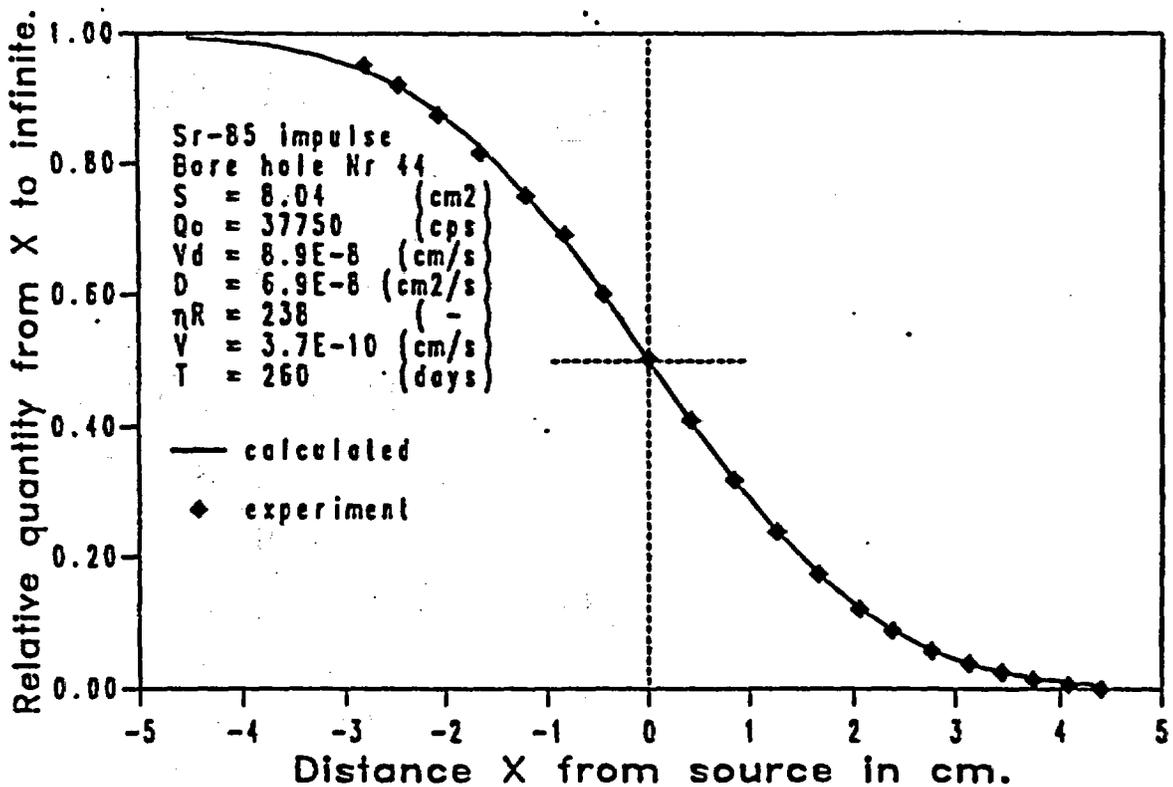


Figure 5. Strontium distribution in the clay core of borehole 44 after 260 days of water percolation

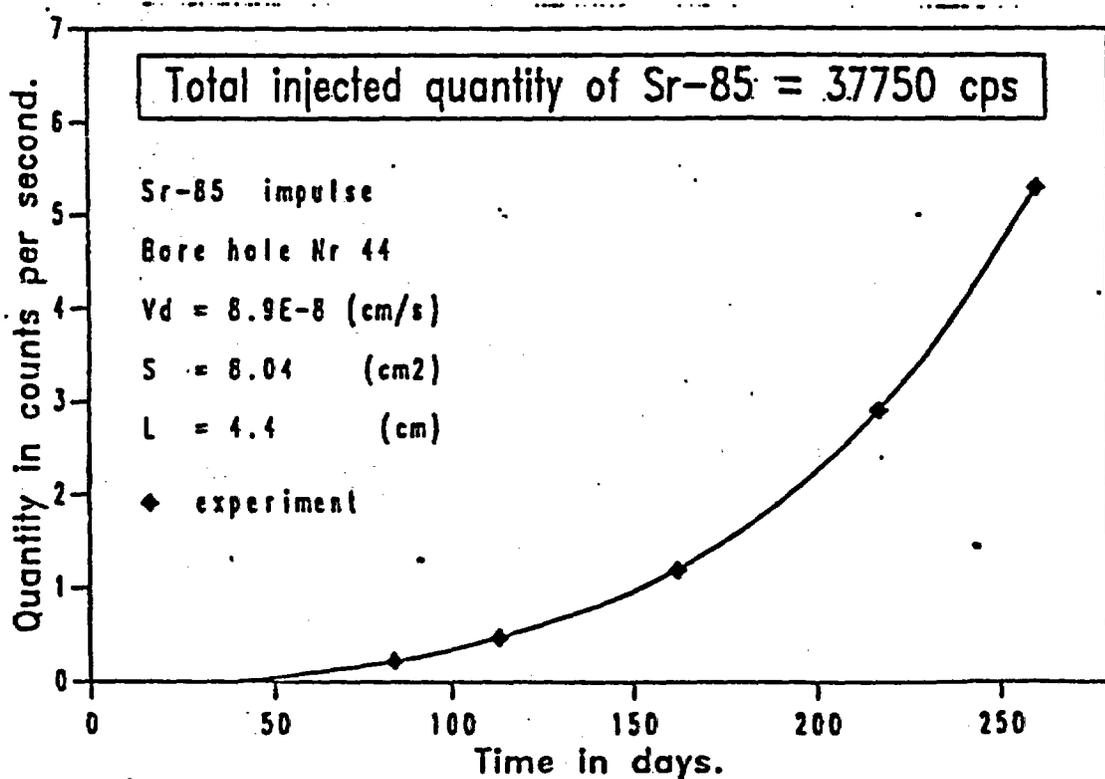


Figure 6. Total quantity of Strontium transported through the clay plug of borehole 44 by the combined effect of advection and diffusion

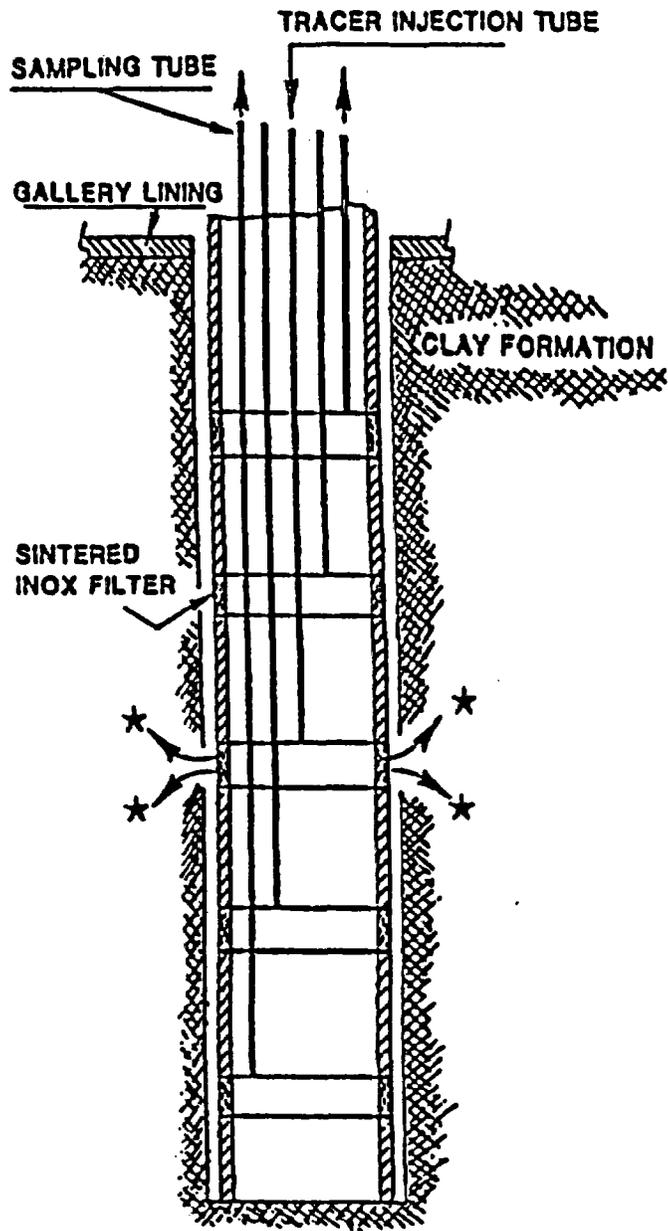


Figure 7. Diagram of in-situ tracer injection system at MOL
(CEN/SCK, 1988)

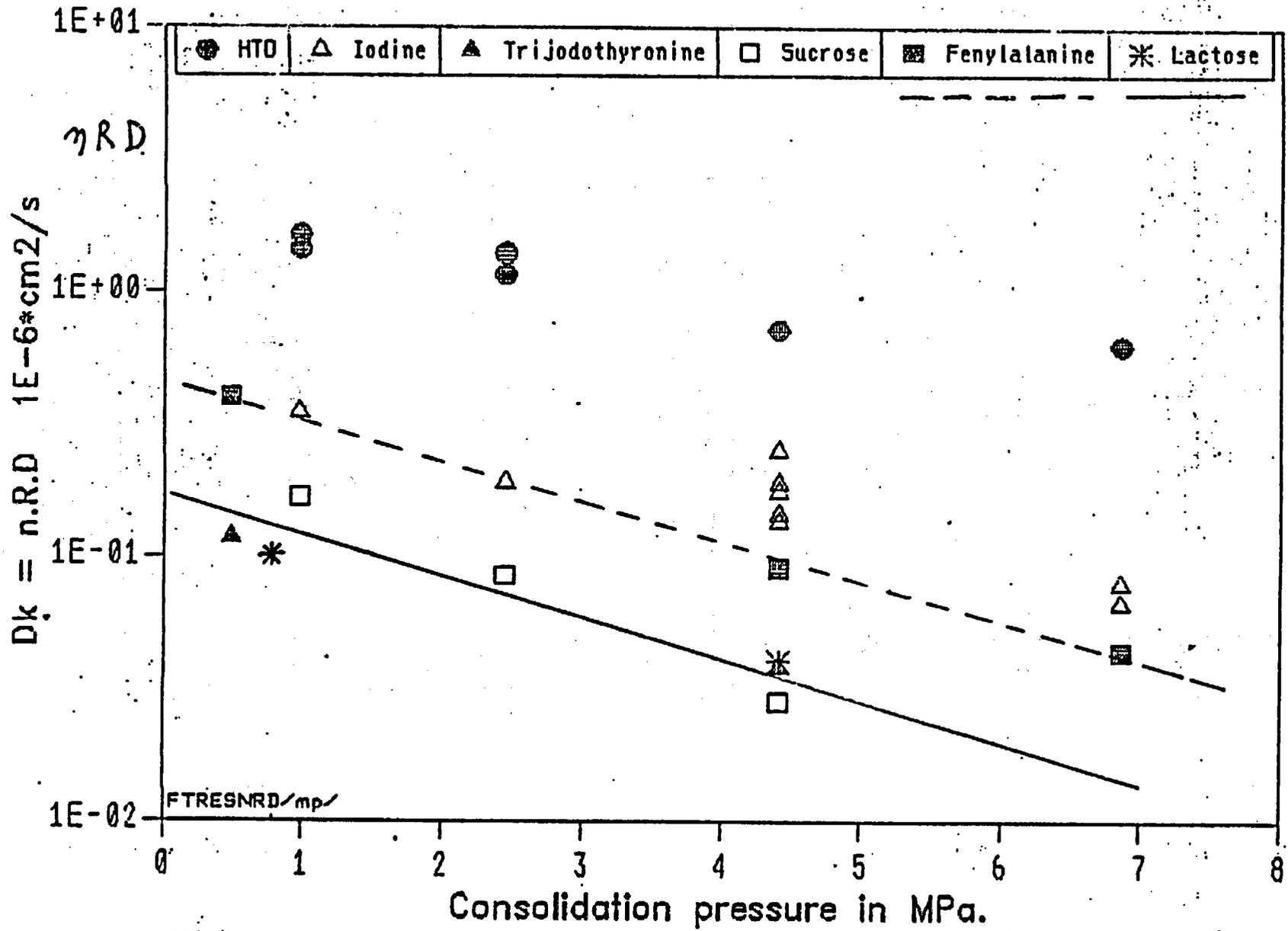


Fig. 8: Influence of consolidation pressure on n.R.D

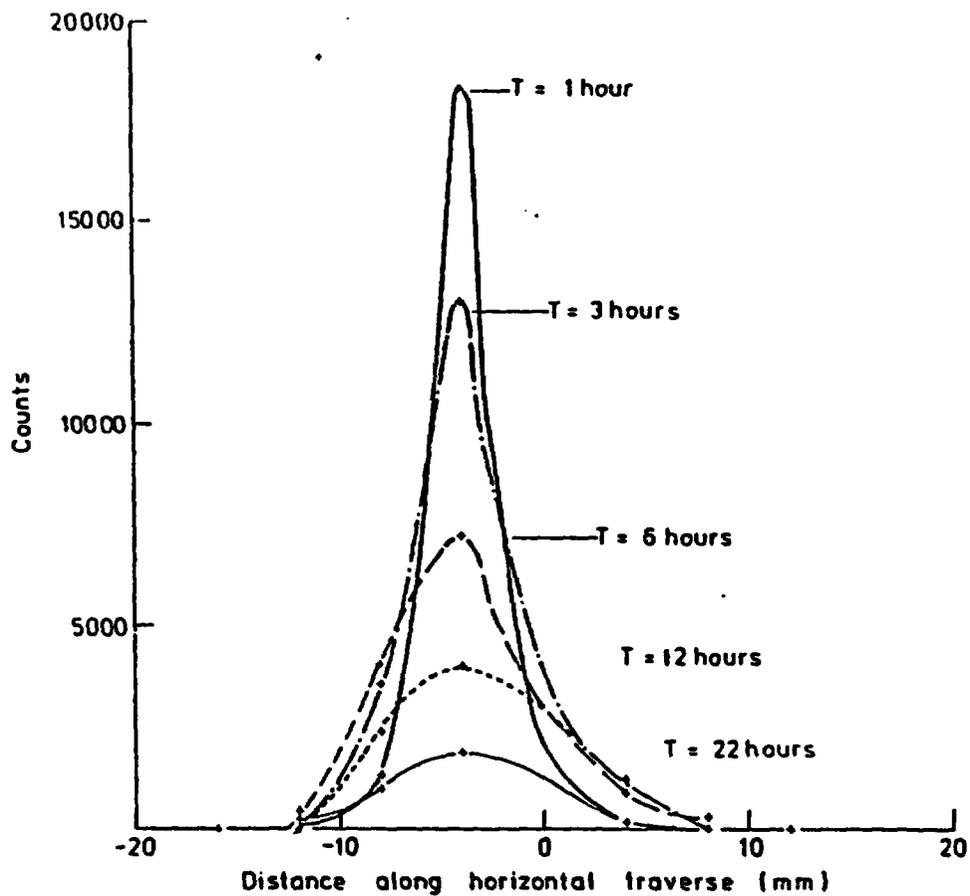


FIGURE 9. MIGRATION OF I-131 IN A BLOCK SAMPLE OF BOOM CLAY

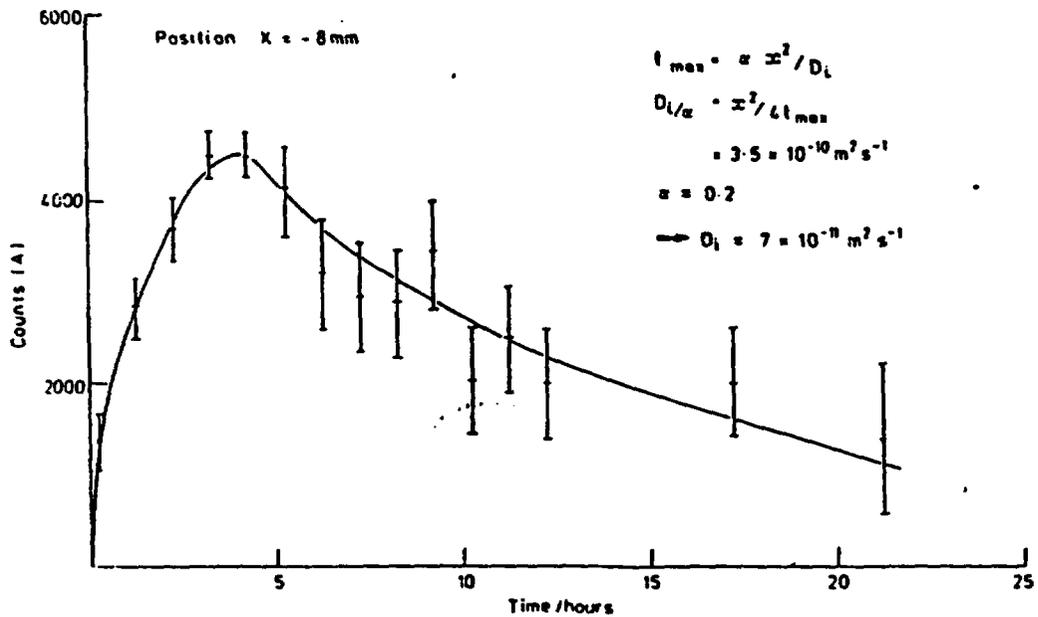


FIGURE 10. COUNT RATE AT A DISTANCE 4.5 mm FROM INJECTION POINT AS A FUNCTION OF TIME.

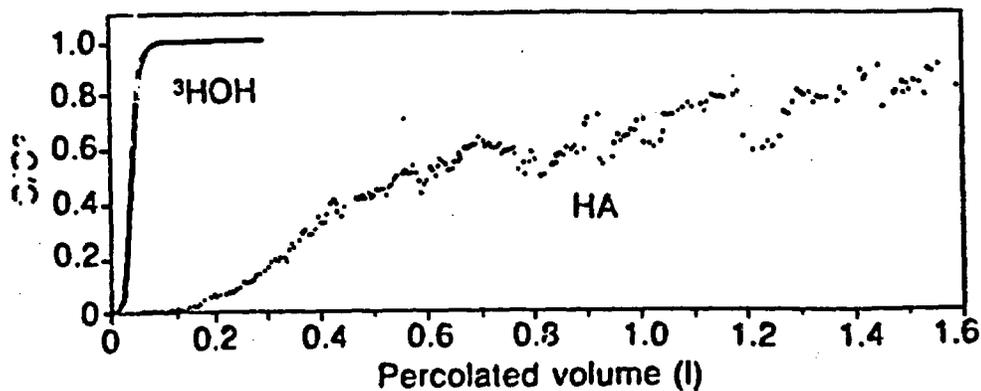


Fig. 14 - Column breakthrough curves for tritiated water and HA suspension in groundwater (25 ppm). Column length: 19 cm. Flow rate: $1.5 \text{ cm}^3 \text{ h}^{-1}$. $E_h \leq -200 \text{ mV}$.

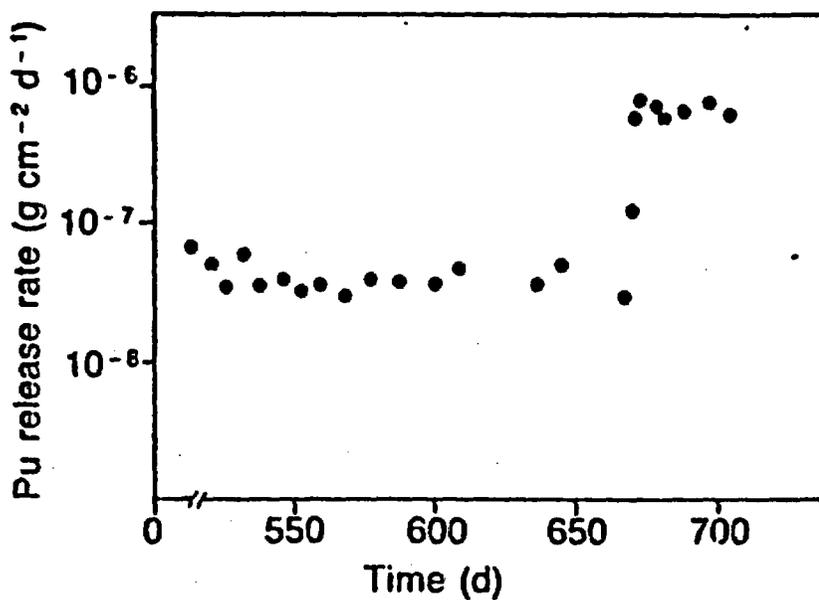


Fig. 15 - Time dependence of the normalized release rate of ^{238}Pu from borosilicate glass under flow ($1.5 \text{ cm}^3 \text{ h}^{-1}$) and reducing ($E_h \leq -200 \text{ mV}$) conditions. The abrupt increase is associated with the addition of 25 ppm HA to the groundwater.

ATTACHMENT 6

**WORKING DOCUMENT
RESTRICTED DISTRIBUTION**

March 1989

COMMUNITY PROJECT MIRAGE (Second Phase)

Plenary Meeting

Brussels, March 16 and 17, 1989

Review of work done in Research Area

NATURAL ANALOGUES

by

Nell A. Chapman

1. INTRODUCTION

The second, mid-term year of MIRAGE Phase 2 has seen the completion of two of the projects on natural analogues of radionuclide transport and retardation processes, and the incorporation of some new, topical work which was not described in the previous report. The logical structure of this report follows that of the previous year, with the contracts being divided into those concerning diffusion and advection in sediments, and those concerning geochemical transport processes in hard, fractured rocks. The reader is referred to the previous report (Côme, 1988) for introductory explanations of each of the contract aims and methodologies, as these are not treated in detail again in this report.

The nucleus of all international activities in the analogue field continues to be the CEC's own Natural Analogue Working Group, which held its third meeting at a USDOE-hosted workshop in Snowbird, Utah, on the topic of applying natural analogues to performance assessment (Côme and Chapman, 1989). This workshop reflected the increasing focus of analogue studies on producing data relevant for the 'end-users'; now widely recognised as being those charged with presenting the technical cases underlying disposal system performance assessments. The NAWG continues to act as the main international forum for analogue workers and users, and it is encouraging to see much CEC-sponsored work at the core of this 'club'. Past experience in organising analogue studies has been brought to NAWG, and used to great advantage by those setting up new studies. One of the main achievements of the co-operation within NAWG has been to bring a greater degree of objectivity to the presentation and use of data from analogue studies.

2. WORK REVIEW

2.1 Diffusion and advection in sediments

The contracts in this area can be conveniently divided into those dealing with very large-scale, regional movements of fluids and solutes in clays, and those dealing with geochemical transport on the metre to centimetre scale.

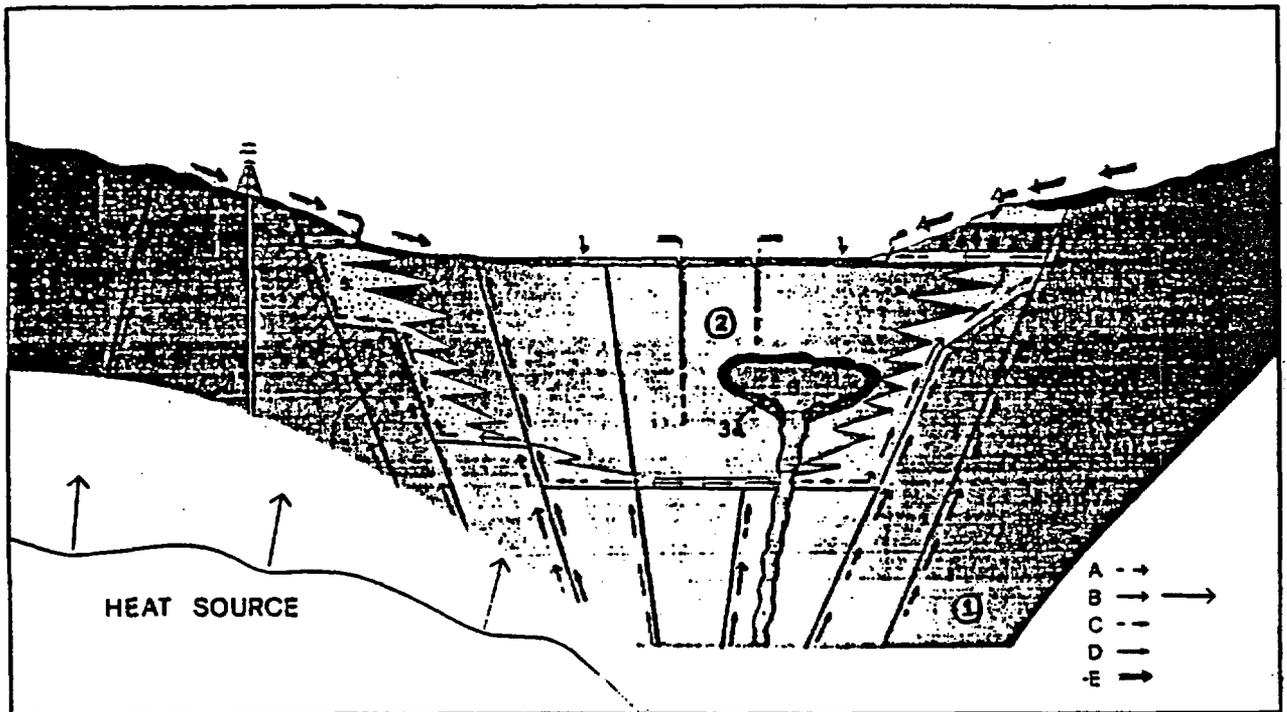
2.1.1. Large-scale fluid movement in clays

Two contracts (Numbers 63 and 71) managed by ENEA (Casaccia) focus a variety of studies on the assessment of large-scale permeability of the Pilo-Pleistocene blue clays of Italy. Over a number of years a considerable observational information base has been built up on the nature of fractures in the clays, the disposition of mineral deposits (e.g. mercury and travertine) and hydrothermal systems related to fracturing and tectonics of the clay-filled basins, the redox behaviour of groundwaters permeating downwards into the clays and, most recently, the relationship between deep-source gases and faulting. This year much of the information was brought together in an illustrated guide (Benvegnu *et al*, 1988) which forms a very useful catalogue of the features and processes available for study. Figure 1 summarises several of these features.

This year effort has been centred on completing the photogeological interpretation of the fault pattern within the Siena basin, and on extended studies of He gas emanation within the basins. The Siena basin is being studied by the University of Siena, which has a sub-contract from ENEA to assess the fracture orientations and densities observed in clay quarries with respect to the orientation of tectonic lineaments within the basin. The photogeological interpretation of the region indicates no obvious features in the central part of the basin, the faulting being limited to the outcrop of the basement, and parallel to the basin margins. Figure 1 shows the significance of the marginal fractures to fluid movement from depth. Further fine examples of the downwards moving redox fronts observed in shallow excavations of the clays and related sediments, and of fracture control of the penetration of oxygen into the reduced clays have been found.

The He soil-gas surveys carried out for ENEA by the University of Rome and reported on last year were extended into two new areas. As described in the previous report, He is produced naturally by radiogenic decay and, in the environment under study here, can essentially be assumed to derive from the basement rocks underlying the clays (97% from the basement; 3% from the clays). This type of rapid reconnaissance work produces maps of He concentrations in soils

Figure 1. Schematic illustration of phenomena under study to assess the large-scale impermeability of the Plio-Pleistocene blue clays of central Italy (Benvegna *et al*, 1988). Fluids of deep origin in the basement (1) reach the surface, largely along the margins of the deep clay basins (2): A- mercury; B- geothermal fluids; C- CO₂; D- He; E- meteoric waters carry oxygen down into the clays. The phenomena include: 3- magmatic intrusion giving rise to thermal alteration (3a) of the clay; 4- the Dunnarobba fossil forest; 5- reduced sand deposits; 6- mercury (cinnabar) concentration; 7- hydrothermal travertine deposits, and; 8- geothermal exploitation. Generally, only He reaches the surface through faults in the clay, all other fluids being focussed around the faulted margins.



which can be smoothed and normalised to highlight areas of abnormally high concentrations indicative of enhanced gas permeability of the immediately underlying sediments. These zones can correspond to deeply penetrating fractures, or areas where a combination of fracturing and lithological variations leads to pathways which penetrate right through the sediments of the basins. The previous studies had been in the Valle del' Era in Tuscany, where He anomalies had been tentatively related to tectonic lineaments in the clay basin.

The first area studied this year was the much larger basin exposed on the east coast of Italy around Vasto, which differs from the smaller, intermontane basin of the Era in being in an area of compressive rather than extensive tectonic stresses. Although the survey was not complete at the time of writing, and the results have not been interpreted, a number of interesting features can already be noted (Lombardi, 1989). First, the overall He concentrations in this region are much higher than the Vall d'Era, at around 2-3000ppb compared to the latter average value of about 600ppb. Second, the largest He anomalies observed seem to be associated with methane concentrations (the basin is a hydrocarbon-rich zone). Third, the anomalies can be related to different styles of faulting in the basin. The older faults trend about NW-SE, parallel to the Appennine chain, while the more recent faults are at right-angles to this trend, and to the coast. Neotectonic studies of the region have been used as the basis for plotting tentative fault locations, and preliminary results suggest that it is these younger faults which are concentrating He fluxes from depth.

A second area now being studied is the Valle del Paglia, which is a southern extension of the Siena basin mentioned earlier. Overall He values are midway between the first two study areas at around 1-2000ppb, and the anomalies so far detected seem to follow two lineaments; N-S and E-W. The pattern of anomalies is quite similar to that observed in the Valle del' Era.

Next year these very interesting studies will concentrate on further interpretation of the data, and on a limited field programme which will complete the Vasto study, and provide linear traverses across each study area. These traverses will also measure CO₂, Rn, N₂, and O₂

levels, and it is hoped to carry out simultaneous measurements of soil permeability to allow further smoothing of the He data. The technique, when further developed, is seen as being a particularly useful means of reconnaissance of areas which might eventually be considered for waste disposal, although it is emphasised that none of the areas currently being studied is being considered for that purpose at present. It is, for example, possible that the technique may be able to give indications of relative ages of faults, as well as their permeabilities.

During the course of the year another interesting phenomenon came to light which may prove useful in the analogue context. Excavation of clay in a brick-pit at Dunnarobba, near Terni, unearthed the remains of a forest with tree stumps and fallen trunks preserved in near original state in a formation of Villefranchian age (0.6-1.5Ma B.P.). These trees (Figure 2), some up to 2m in diameter, and still composed of wood with some minor internal mineralisation, are thought to be tropical species similar to those currently found in Florida, which may have been up to 70m tall. They are preserved in mixed clays and sandy clays, and were apparently inundated when a rapid tectonic change in the level of the lake, along whose shores they grew, resulted in much faster sediment deposition. The clays are generally reducing in character, but oxidised zones occur in the sandier horizons and, where the trees are present at these levels, they can be seen to have caused locally reducing conditions. At present no data are available on the chemistry of the clay pore waters, or the distribution of trace elements in and around the trees. However, two possible courses of study might be:

1. To assess the detailed preservation mechanism for the cellulosic component of the wood in the largely closed geochemical system which has existed for about one million years. This may be of particular interest in safety assessments which are considering the role of organic complexants derived from the breakdown of paper and other cellulosic materials in low-level wastes, and their effects on radionuclide solubilities and transport.
2. To assess the effect of the presence of the organic material in the sandy horizons on the redistribution of U-series radionuclides which may have been mobile in the shallow

Figure 2. Photograph of the Dunnarobba fossil forest, Montecastrilli, Umbria, shortly after its discovery. The height of the tree stumps, which are still composed of wood, is up to 3m.



groundwaters. These could be compared directly to the results found by BGS in much younger sediments where organic debris has either concentrated U, or reduced surrounding sediments so that they concentrate U (see next section).

Quite apart from the He studies, which are showing the great potential of the technique, there is clearly much work which could be done to utilise the wealth of information which has been accumulated on the Italian clays. It would, for example, be very interesting to study detailed profiles of pore water chemistry and isotopes in drill cores which penetrate the clays in various zones; centrally in low permeability areas of the basins, around enhanced permeability regions as indicated by the He anomalies, in and across deeply penetrating fractures, etc. This type of study would allow a picture to be built up of long-term mobility of elements as sedimentation occurred and the basins evolved, and would provide much-needed insight into solute transport processes in clay-rich sediments, where models and concepts are still poorly developed.

2.1.2. Smaller scale elemental migration in sediments

This area is covered by two main programmes of work, the BGS/EMP work (contracts 73 and 70) on recent (1000-10,000 years old) land-based sediments associated with adjacent sources of natural series radionuclides in older U mineralisation, or with distinct geochemical discontinuities in the sediment layers, and the IOS studies of similar discontinuities associated with U-rich redox fronts in deep sea sediments. Both studies are aimed at modelling elemental speciation and mass-transport on a scale of cms to a few tens of metres.

The British Geological Survey studies are focussed on three sites in Scotland (Hooker, 1988), and are supported by collaborative contracts covering geochemical modelling aspects with Ecole des Mines de Paris and Atkins (UK). As presaged in the last report, work at the Lundin Castle site has been discontinued, and contractual modifications have now brought work which has been underway for two years at the Broubster site into the MIRAGE programme. The aim of all the studies is to provide data on the speciation of natural series radionuclides and iodine in groundwaters in sediments, their mobility

and the retention processes which are operative, and to use this information to calibrate or validate speciation and transport codes. Part of the work, completed early in the year, was a review of the potential significance of surface diffusion (Cook, 1988), with particular emphasis on clays. It was concluded that the mechanism may be highly significant, and the report highlighted the paucity of data on the effective porosity of clays, and our limited understanding of the real transport mechanisms governing cation migration. A number of experimental approaches to testing surface diffusion models were suggested.

At the Loch Lomond site, which featured in MIRAGE phase 1, work to characterise the behaviour of iodine in the lake-bottom sediments got underway again in September 1988 when a fresh core was taken. Prior to this the SURRC had been developing and testing an extraction and analytical procedure to assess iodine speciation and location in both solid and pore-water phases. Core sub-samples have now been centrifuged to abstract the pore-waters, which have been passed through a HPLC system to produce a series of various molecular weight fractions of the inorganic complexes present. These have been subjected to neutron activation for analysis and the first results are expected shortly.

Much of the work in 1988 has focussed on the Needle's Eye site in Kirkcudbrightshire. The disposition of the sediments under study was illustrated in the previous report. Four pits have now been examined in the sediments below the cliff, and a clearer picture of the hydrology and geochemistry of the site is emerging. Figure 3 (Roberts, et al, 1988) shows the current interpretation of water movement in the site. In simple terms, waters which have percolated through the U-vein in the cliff mobilise U, probably as U^{6+} carbonate complexes, and pass over the sediments, allowing natural series elements to *diffuse* downwards. As can be seen from Figures 4 and 5, a certain amount of U has been fixed on the humic rich organic layer at about 0.5m depth, where the organic content of the sediments is about 12%. The more significant U peak at about 1.2m depth is thought to result from the upwards *advection* of radionuclides from a flow of oxygenated water which has also passed through the vein system in the cliff, but which moves relatively swiftly along the sediment-bedrock interface, or in more permeable horizons in the lower part of the sediment pile, both

Figure 3. Schematic diagram of water flow at the Needle's Eye site. Surface water which has passed over or through the U-vein in the cliff allows downward diffusion of U into the upper zone of the sediments. Both piezometric data from boreholes in the sediments, and the regional flow modelling, indicate upward movement of groundwater which has passed through the vein zone in the hornfels, into the base of the sediments where the water moves laterally to the sea along high permeability silty horizons. This provides the second input of natural series radionuclides to the sediments.

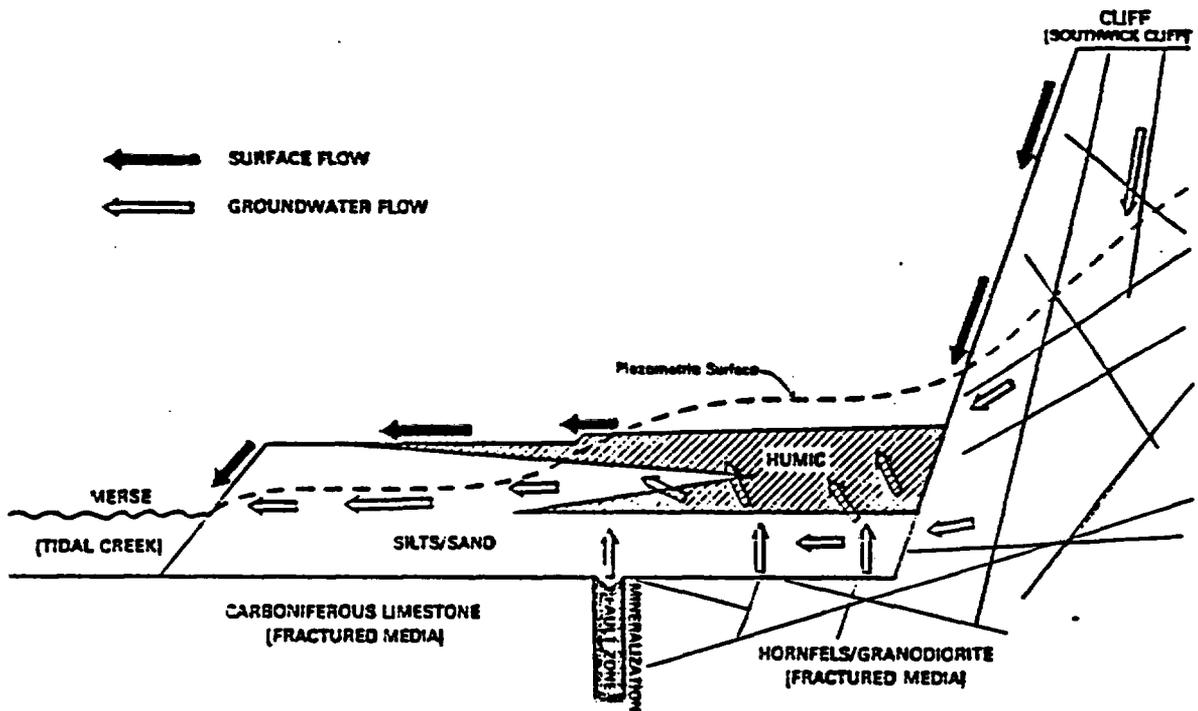


Figure 4. Cross-section of a pit profile through the Needle's Eye sediments. Note the upper peat horizon, and the main silty layer between 90-150cm depth.

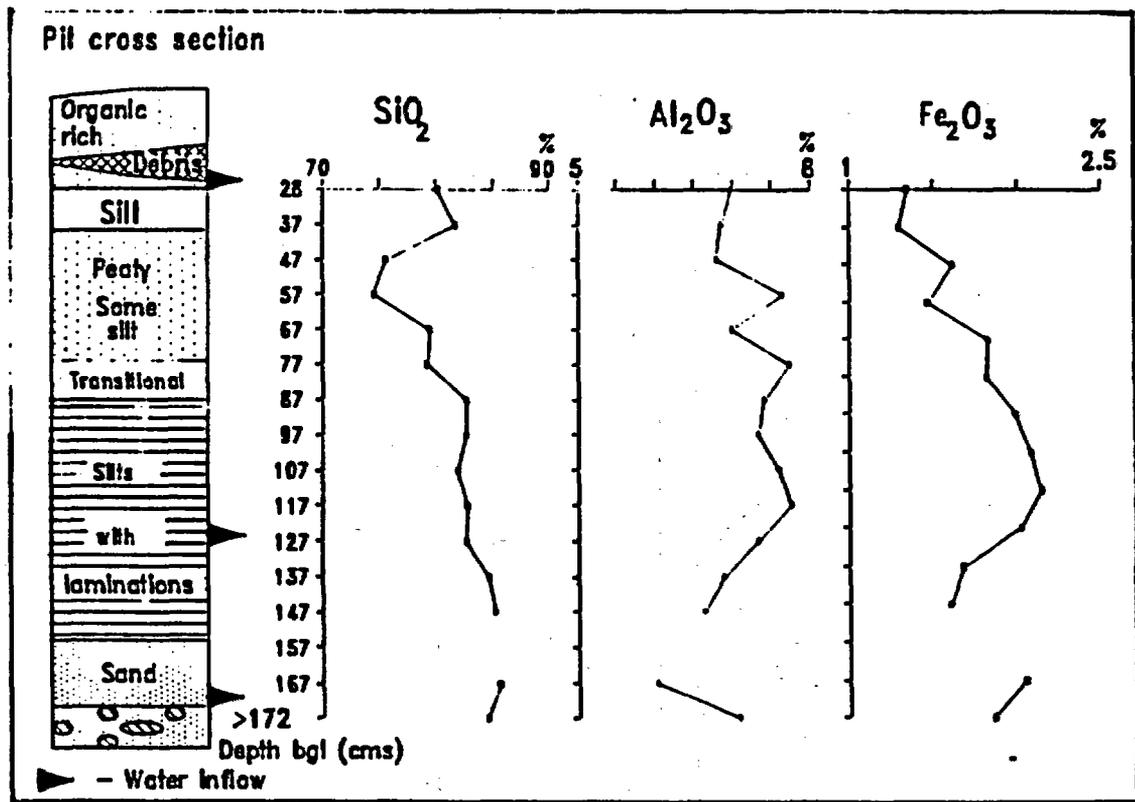
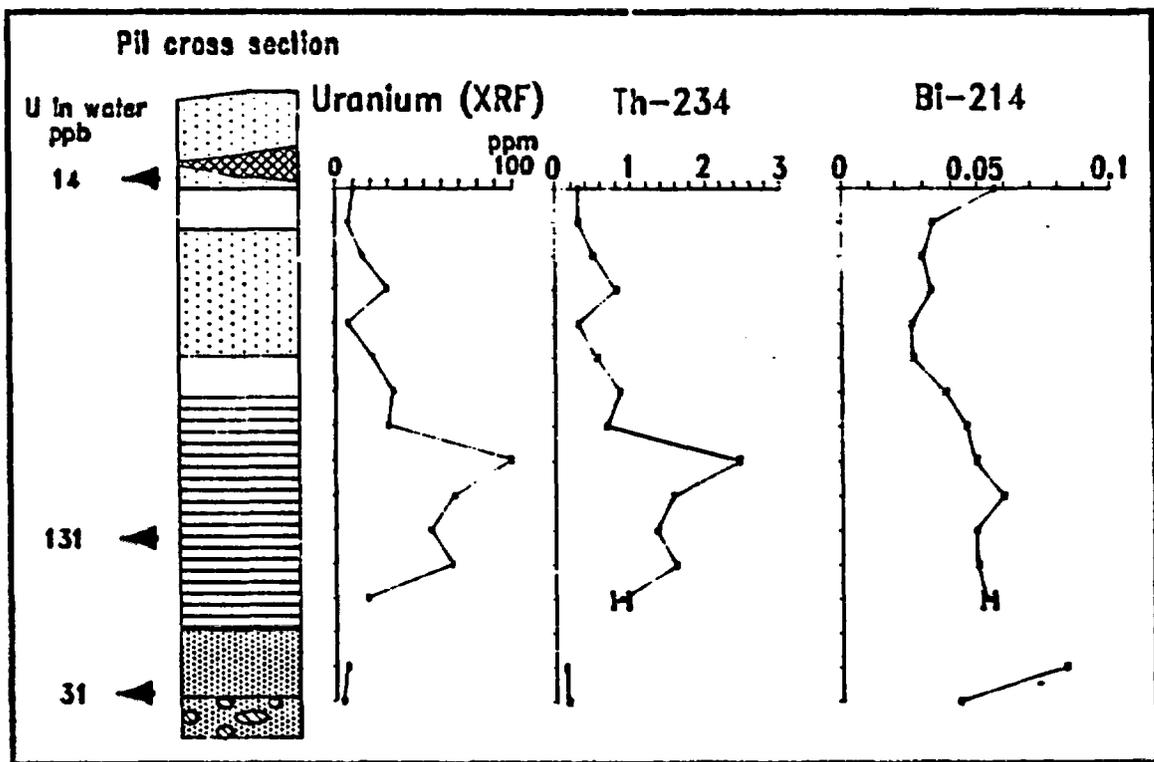


Figure 5. Natural series radionuclide concentrations in sediments, showing the two peaks at about 50 and 120cm depth. Arrows show U concentrations in the three main inflowing waters.



of which have high piezometric heads. The mineralogy of the sediments suggested that the U had been sorbed onto Fe-oxyhydroxides in this zone, but very recent autoradiographic data show the U to be associated with the limited (~2%) amount of organic material in this horizon. In detail, it can be seen that U is associated with organics at all levels in the sediments. In the upper levels it forms haloes around root channels, and is associated with fine organics in the matrix of the sediment only, not on large fragments of plant debris. At the ~100cm level, however, it is very strongly associated with large pieces of organic debris. The U in the sediments is strongly out of equilibrium with its daughter radionuclides, ^{214}Bi , ^{208}Tl , and ^{212}Pb , suggesting that it has been transported without them and they are now growing back into the system. In contrast, Th is only found to be present in resistate heavy mineral fractions, where it is in equilibrium with its daughter radionuclides, and has been immobile.

These 'solid-phase' data have been linked with information on the porewater chemistry, in particular with data on the types of organic material in the waters derived from sequential extraction ion-exchange columns, operated in the field. Near the cliff base the organics are very hydrophobic with little ionic character; there is no evidence of humic/fulvic acids and the organics are probably hydrocarbons leached from the metamorphic rocks. Such organic species would not complex with U, so organic transport of U from the vein can be ruled out. At a depth of 1.2 to 1.6m in the sediments further away from the cliff the TOC content is low (3-5ppm), comprising uncharged hydrophilic species, probably the oxidised hydrocarbons. At greater distance from the cliffs and at similar depths, near the base of the sediments, classical ionic humic/fulvic material is found, although TOC is still only 3-7ppm.

Preliminary speciation modelling supports the view that U is mobilised from the vein in the cliff as anionic carbonate complexes such as $\text{UO}_2(\text{CO}_3)_3^{4-}$ or $\text{UO}_2(\text{CO}_3)_2^{2-}$ which, under oxidising conditions, probably sorb onto Fe-oxyhydroxide coated surfaces which, at the low pH of the waters (<8) would be positively charged. Under reducing conditions the uranium would be present as UO_2^{2+} and would sorb easily onto organics, or may be present in the waters as U^{4+} (EDTA)-type organic complexes. When data are available on the U-content of the extracted organics, this modelling can be tested.

Some laboratory R_D data have been obtained for the sediments, which indicate that a minimum value for U on the silty sediment layers should be about 60ml/g, and on the peaty horizons, >10,000.

Initial geochemical modelling by EMP (Jamet, et al, 1988), which used groundwater data only in the CHIMERE code linked to the CHEMVAL database, as no detailed mineralogical data were available at the time, suggested that the U in solution in the groundwaters (at around the 15-150ppb level) was controlled by the solubility of liebigite, $Ca_2UO_2(CO_3)_3 \cdot 10H_2O$, while the major element chemistry of the waters suggested precipitation of $NaHCO_3$. The mineralogical data (Basham and Hyslop, 1988) are at odds with this, however, as U is present in oxide and silicate forms only, and no bicarbonate is present in the sediments. This highlighted a problem with the CHEMVAL/PHREEQE database, in that it contains very limited data on silicate minerals, which limits its usefulness for modelling real geological systems. This is slowly being rectified, but more data are needed, particularly on clay minerals.

Recent developments in the EMP modelling have been the building of a more refined 2-D groundwater flow model at three scales, from a regional one of 1500m length, to a local one describing the cliff-bottom region. The database for Needle's Eye is now adequate for more detailed modelling, which will comprise the closing stages of the project next year. In particular it is hoped to be able to bring together the sorption, data with the hydrochemical, mineralogical and hydrological data to perform mass transport calculations, using the STELE code (STELE = CHIMERE + METIS). It is proposed to try further validation of the CHIMERE model and the CHEMVAL database by a series of runs which predict, for example, pH values in the various sediment zones for comparison with field values. In a first trial, METIS will be used in combination with the R_D data to assess transport. A more sophisticated approach will then be taken, using STELE with its facility to look at surface complexation processes, to model transport and retardation as an equilibrium process. For these trials it will be assumed that the sorbing surfaces are Fe-oxides, behaving like goethite. An initial source term is required for all the transport modelling, and the SURRC data on natural series disequilibria in soils overlying the vein on top of the cliff can be used to formulate this.

Although the $^{234}\text{U}/^{238}\text{U}$ ratios in samples at various distances above the vein tell no story, the $^{230}\text{Th}/^{234}\text{U}$ ratios show very strong evidence of preferential U leaching close to the vein (ratio of ~3) by lateral flow along the rock-head. The latter ratio is reflected in the values from the vein itself (~1.6).

The Broubster site in Caithness, Scotland, is new to MIRAGE. The site comprises a zone of U, Pb and Zn hydrocarbon-containing mineralisation in the Caithness Flagstones (sandstones, limestones, siltstones), overlain by thin silty soil. Downhill from the site (to the east in Figure 6) the soil thickens and becomes more organic-rich, eventually turning into a saturated peat deposit. Soil samples show that the U has been preferentially mobilised from the deposit and advected in the soil zone before being trapped in the peat about 100m down gradient, whereas Pb and Zn have remained immobile. The site has been excavated and sampled for soil, rock and waters (Read and Hooker, 1988) with a view to examining, in particular, the role of organic species in the transport of U. The U, Th and REE's are concentrated strongly in the peat layer (Figure 7), with U up to 1200ppm, compared to values of around 15ppm around the deposit itself, and total REEs up to about 750ppm. U levels in the strongly oxidising and slightly acidic waters reach 21ppb above the deposit.

The hydrochemical data from the site have been modelled using the PHREEQE code with the CHEMVAL database, using surrogate data on humic substances from Shanbhag and Choppin (1981) in the temporary absence of characterisation of the Broubster organics. In summary, the model showed that U^{6+} is the dominant oxidation state throughout the system, with U being transported in the soil waters as a neutral carbonate complex. Concentrations of only 100ppb of HPO_4^{2-} would be enough to make phosphate the dominant transport complex. All the waters are unsaturated with respect to common uranium minerals so U concentrations are not solubility controlled. As pH decreases, when the U is transported into the peat zone where pH drops from about 7 to about 5, then the model predicts that a humate complex, UO_2HA^+ , will become dominant (Figure 8). Running PHREEQE with different databases produced various levels of significance for the pH range of humate complexation. The NEA/EIR database was used to model Th, which was predicted to be present dominantly as a neutral $\text{Th}(\text{OH})_4^0$ species, with

Figure 6. The Broubster site in Calthness, Scotland. The mineralised zone to the west (left) of the road has retained Pb and Zn, while U has been washed down the slope and reconcentrated in a peat marsh to the east of the road.

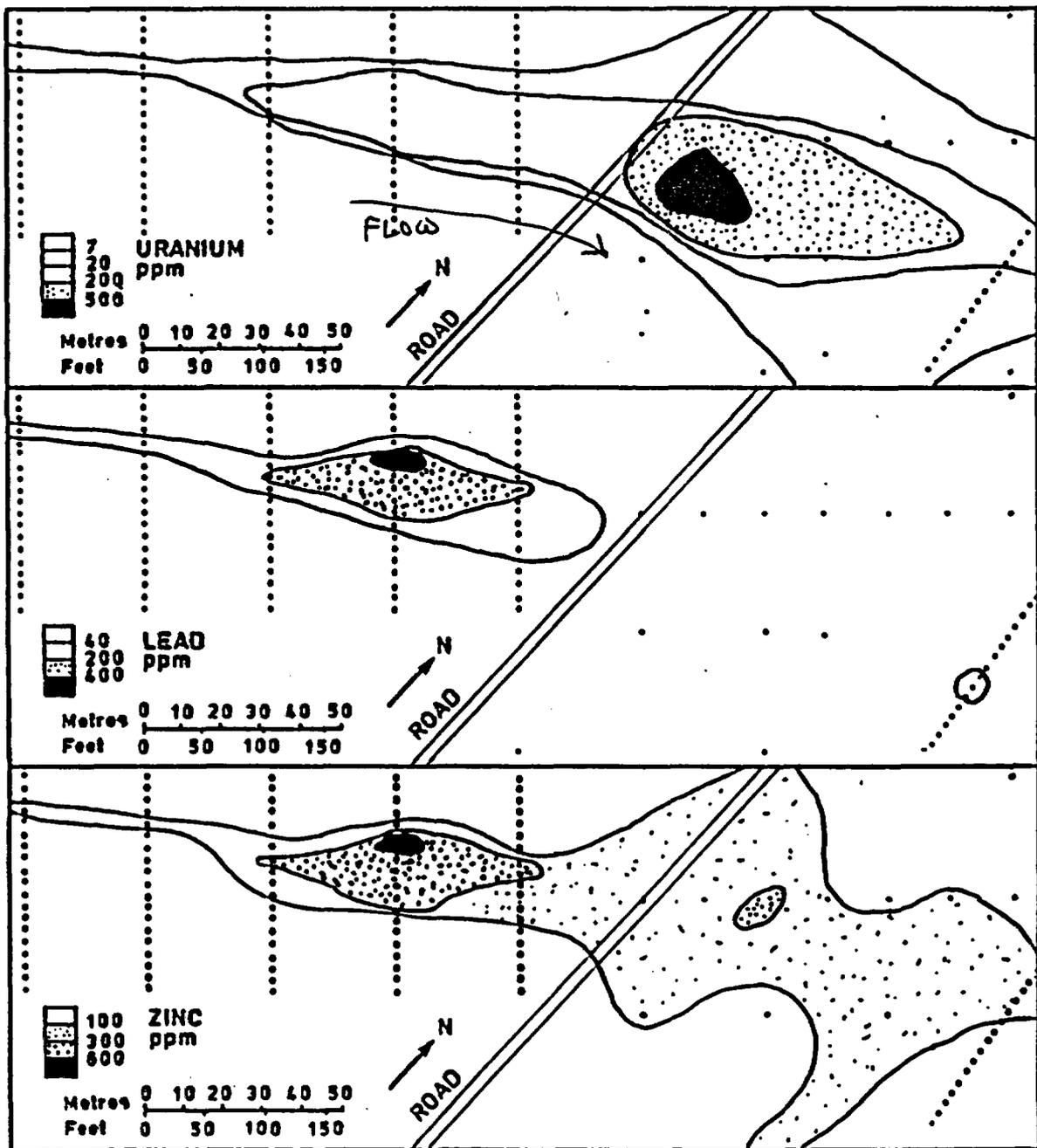


Figure 7. Profile of a pit in the peat marsh (U-deposition) area at Broubster, showing natural series radionuclide concentrations in the solid phase. Peat (horizon A) overlies boulder clay with a leached top (E) from which Fe has been flushed down into horizon B/C.

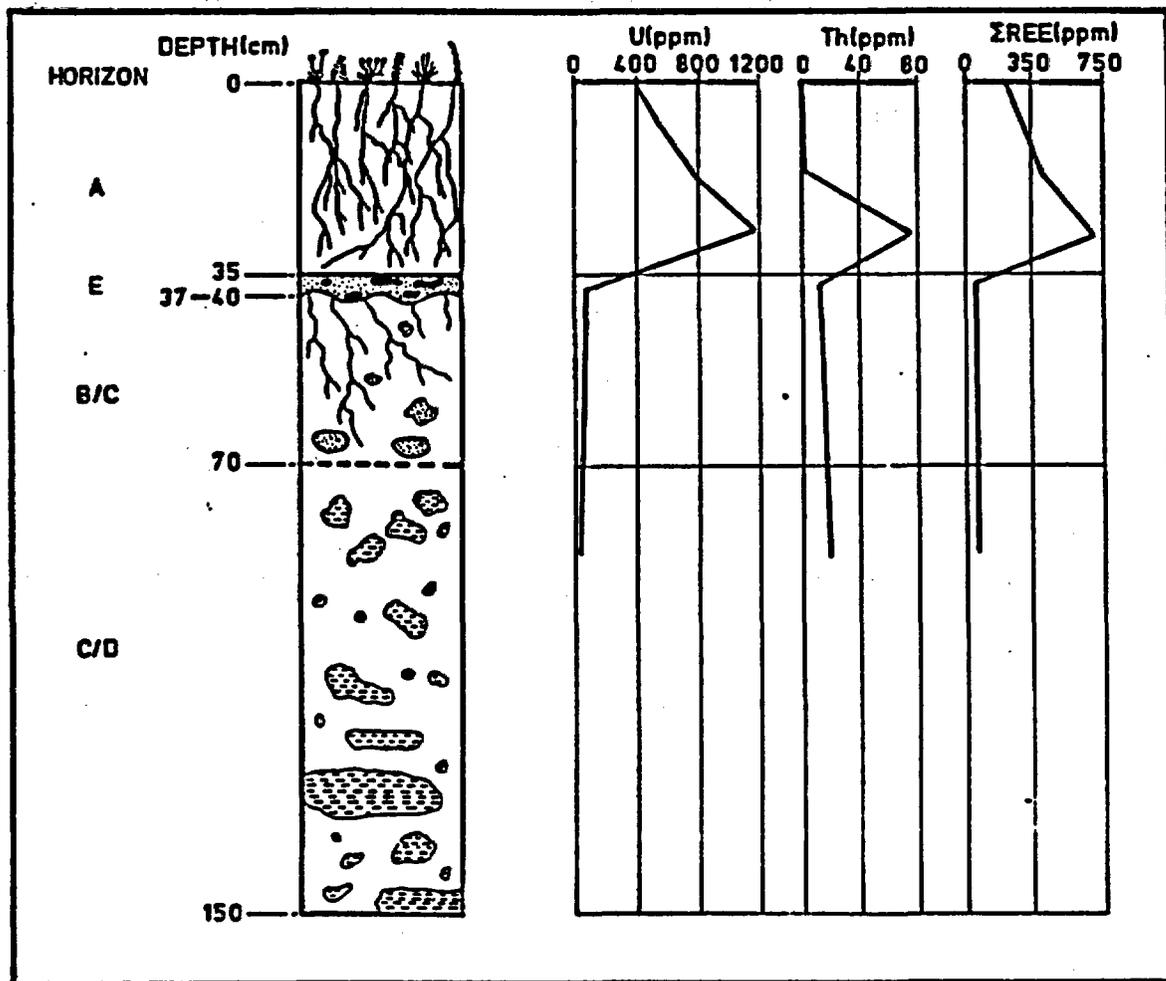
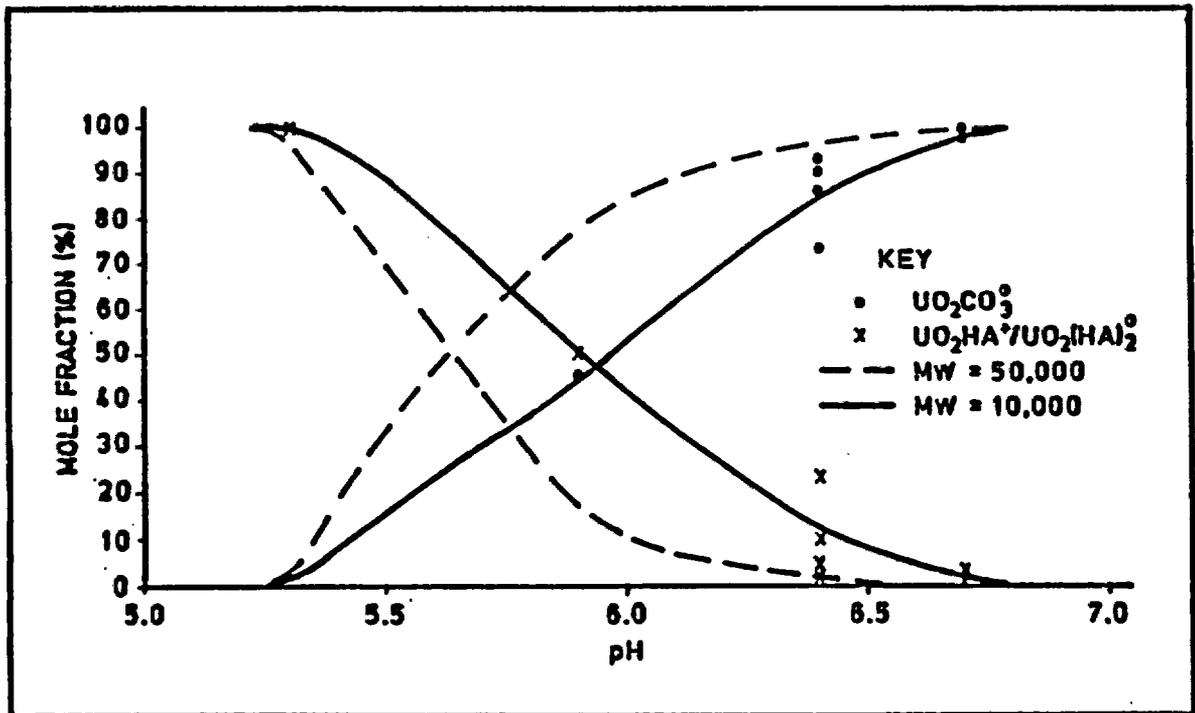


Figure 8. Predicted stabilities of uranium carbonate and humate species in Broubster groundwaters, as a function of pH, derived from the PHREEQE code.



levels controlled by the solubility of an amorphous oxide phase. Since amorphous $\text{Fe}(\text{OH})_3$ is also calculated to be saturated in the groundwaters, co-precipitation would be expected to remove all Th from solution.

These results were partially tested using the BGS 'speciation rig', the portable column extraction system to isolate cationic, anionic and neutral species from groundwaters mentioned earlier in the Needle's Eye report. The majority of U was indeed bound to organic matter, and Fe-oxyhydroxides are responsible for retention of much of the Th, but poor mass balances indicate that a colloidal Th phase may be present. The modellers concluded that if the field data on U speciation were verifiable, then it would indicate that the CHEMVAL database will tend to underestimate the strength of U-humate complexation. Other databases had the opposite effect, and this is a fine example of how analogue data can be used to test both the models and the databases in the real world.

The tentative model for transport (Figure 9), which is to be refined in the coming year, thus has U being mobilised, then rapidly oxidised and transported as a carbonate (or possibly phosphate) complex and, on hitting a pH front, switching from these neutral/negative inorganic complexes to positively charged organic complexes which are strongly sorbed by the peat. Th, on the other hand, is probably transported as colloidal oxy-hydroxide which easily co-precipitates with iron.

The IOS study (contract number 146) of uranium series radionuclide behaviour in deep sea sediments from the Madeira Abyssal Plain (Atlantic Ocean) entered its second year. The early part of the year was spent in refining extraction and analytical procedures to make best use of the core material available from two boreholes, MD10 and MD24. Originally it had been hoped to determine concentrations of all the radionuclides of interest (^{238}U , ^{234}U , ^{230}Th , ^{231}Pa , ^{226}Ra and ^{210}Po) using a single sample of each depth interval concerned, but in the event ^{226}Ra had to be determined separately.

The mechanism of turbidite formation which leads to the fossilisation of redox fronts in successive turbidite horizons in the sediment cores was elaborated in the previous report. Figure 10 recapitulates the geochemical background to this process. The principal objective of

Figure 9. Conceptual model of U/Th and REE transport at the Broubster site. See text for explanation.

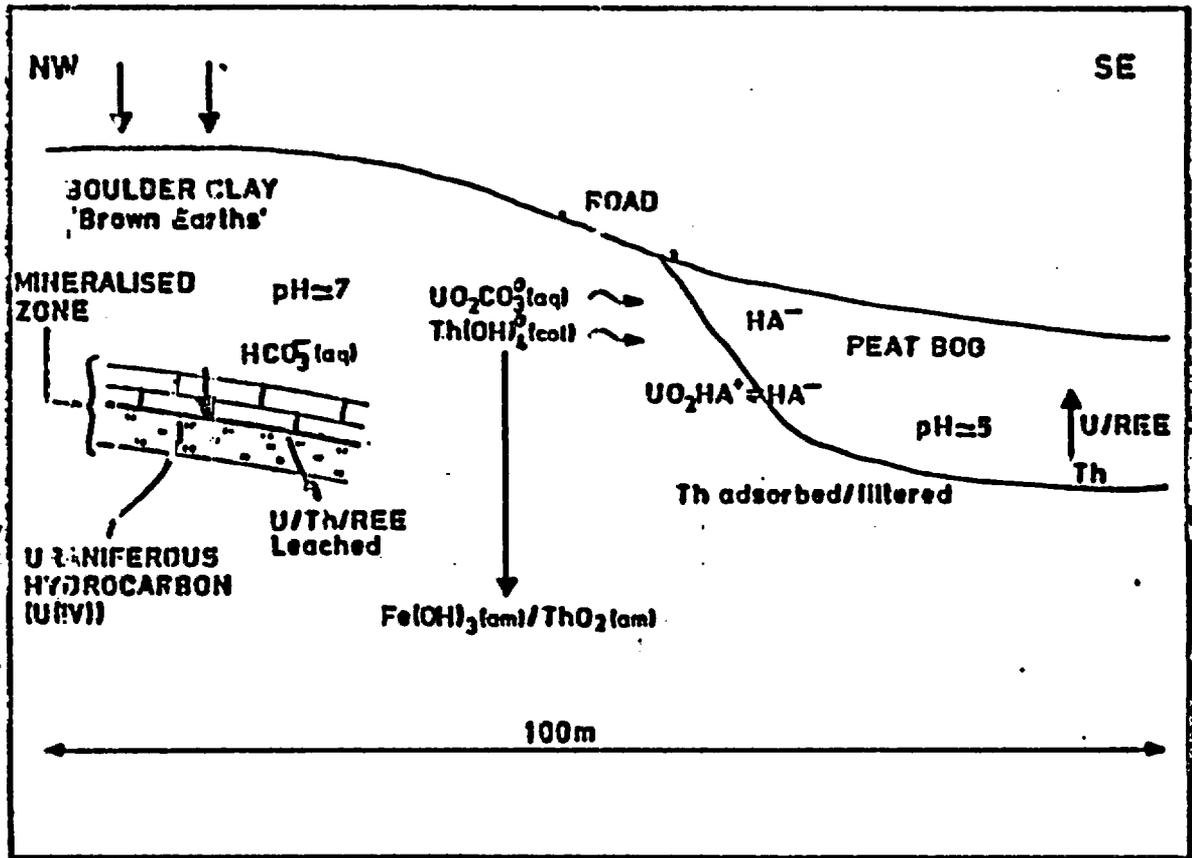
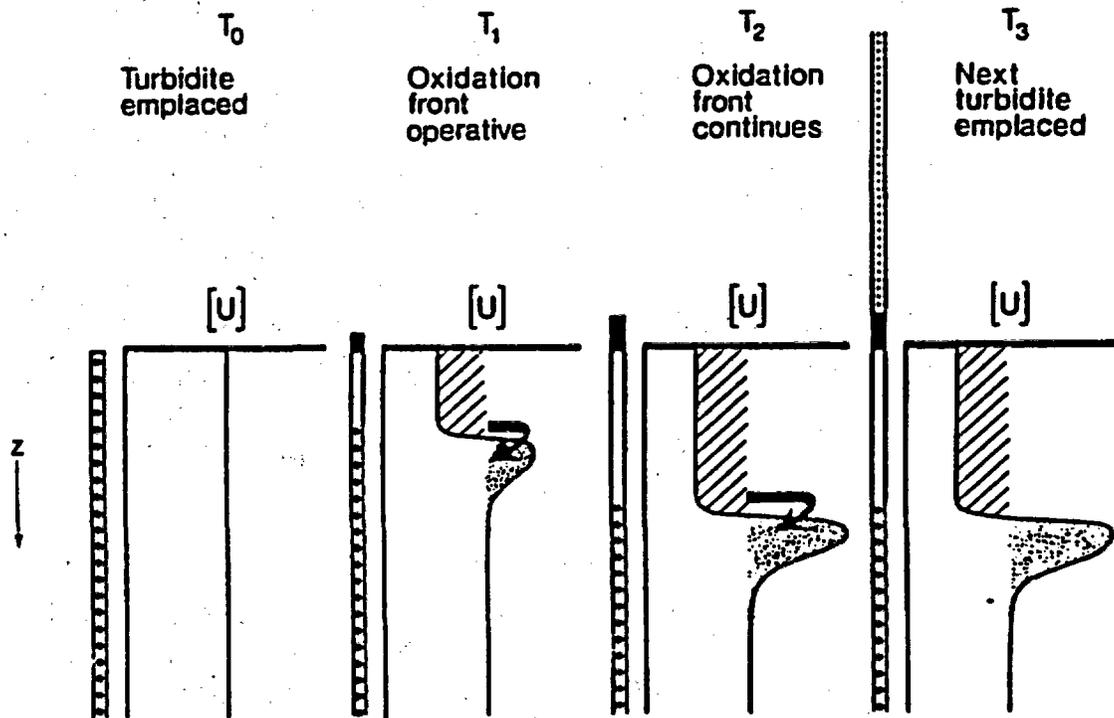


Figure 10. Schematic representation of the formation of diagenetic uranium profiles in Madeira Abyssal Plain turbidites (Colley, et al, 1988). At T_0 the newly emplaced turbidite has uniform distribution of U in detrital and authigenic phases. At T_1 oxygen from ocean-bottom water has diffused into the turbidite, oxidising organic carbon and mobilising authigenic U only. A small quantity of pelagic sediment has accumulated on top of the turbidite (black portion of column), and a fraction of the mobilised U has formed a peak below the moving oxidation front (shown as black dots in the column). At T_2 the front has moved further into the sediment and mobilised more U which has moved with it. At T_3 another turbidite has been emplaced on top of the pelagic sediments, stopping the progress of the redox front below as access to oxygen from the ocean water has been cut-off. The U peak remains fossilised, and can act as a source for later diffusion in pore waters under suitable conditions.



this study is to use the fossilised redox fronts as analogues for a concentrated source of radionuclides (such as a waste container buried in clay-rich sediment) from which diffusive migration could occur over a well constrained time period in stable geochemical conditions. In addition the system can be used to assess the general mobility of U-series radionuclides in a non-advecting environment, and to examine more general issues concerning the way in which redox fronts can act as 'secondary source terms' in far-field transport calculations.

The previous report described the results of preliminary work on turbidite *t* in core MD10. This year work has extended to look at other turbidite horizons and the second core, MD24. As can be seen in Figure 11 the turbidite units can generally be traced from one core to the next. The main units of interest are *s*, *t*, and *w*. In core 10 it can be seen that two additional thin turbidites (*s*, and an un-named unit) are present between *s* and *t*, deposited at a time when only normal pelagic sedimentation was occurring at the site of core 24. The arrival of the first of these clearly had a marked effect on the underlying unit, *t*, since it can be seen that it has no characteristic redox front with associated colour change and U enrichment peak. Consequently it is assumed that this un-named turbidite arrived shortly after unit *t* itself, and sealed it from downward diffusion of oxygen. These new results have resulted in a change of emphasis of the work away from unit *t* in core 10, towards unit *s* (in either core), and units *t* and *w* in core 24. However, the rather interesting processes which occurred in core 10 between the two main units may provide some very useful data, and will be studied further next year.

Extensive data have now been accumulated on unit *w* in MD24. Figure 12 shows the profiles for members of the upper part of the ^{238}U chain, which support the earlier findings that the system seems to have been radiochemically closed since it was sealed more than 700,000 years ago. The downwards diffusion of the U peak away from the relict redox front is clear. Essentially this diagram tells us that there has been no preferential mobility in the decay sequence $^{238}\text{U} \Rightarrow ^{234}\text{U} \Rightarrow ^{230}\text{Th}$. However, as can be seen in Figure 13, this closure breaks down at ^{226}Ra , and both it and ^{210}Po have distributions that do not coincide with the other peaks. It is assumed that this is a result of Ra being mobile in the Ra^{2+} state. The immobility of ^{234}U indicates that even if this daughter were born into the pore-water phase by recoil, it has

Figure 11. Stratigraphic logs and solid-phase U profiles for cores MD24 (left) and MD10 (right) from the Madeira Abyssal Plain turbidites, showing the correspondence between turbidite units.

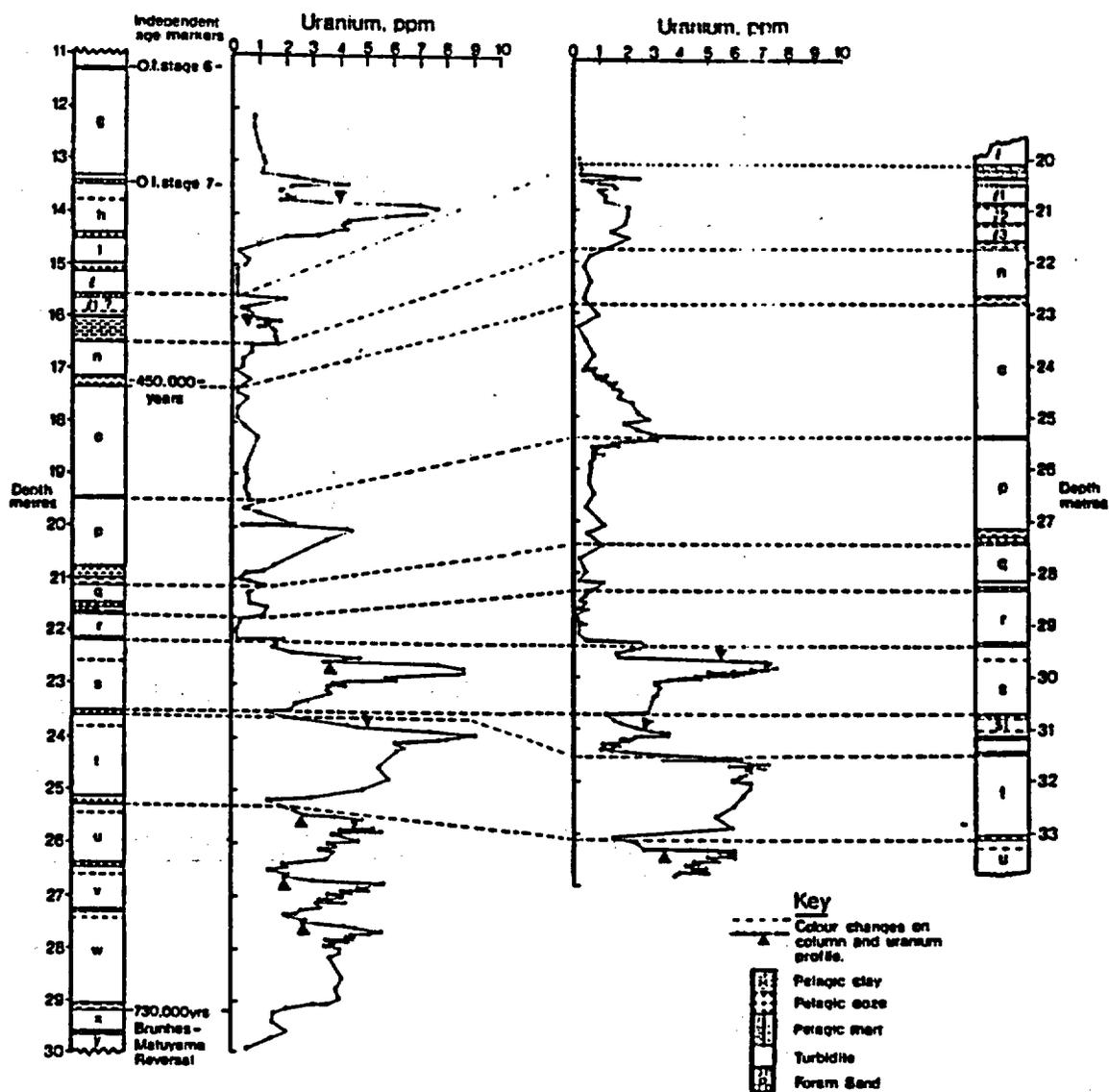


Figure 12. Natural series radionuclide distributions in turbidite w and surrounding units (see Figure 11 for correlations) in borehole MD24. The shaded areas are pelagic sediments between consecutive turbidites, and the horizontal line shows the position of the relict redox front in unit w. The radiochemical closure of the system for these upper members of the ^{238}U chain is clear (diamonds = ^{238}U ; crosses = ^{234}U , and triangles = ^{230}Th ; the latter points being joined to show the profile).

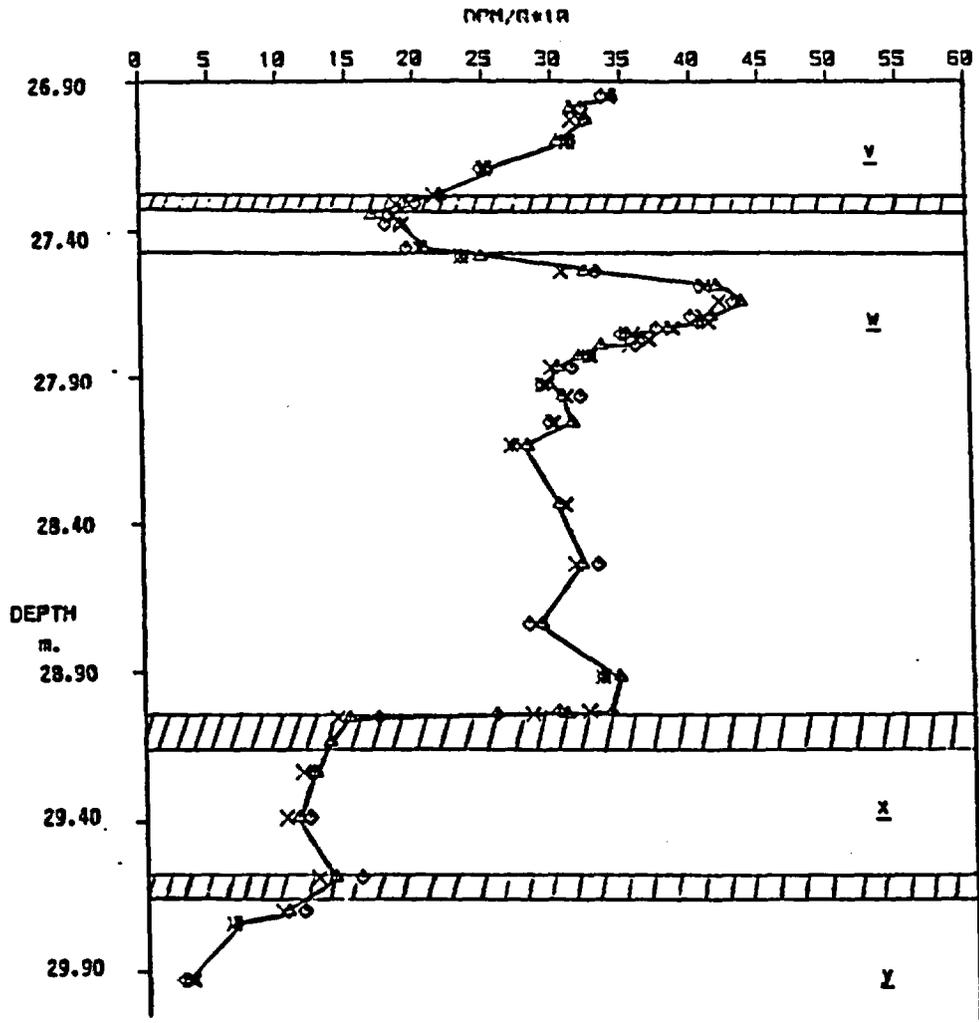
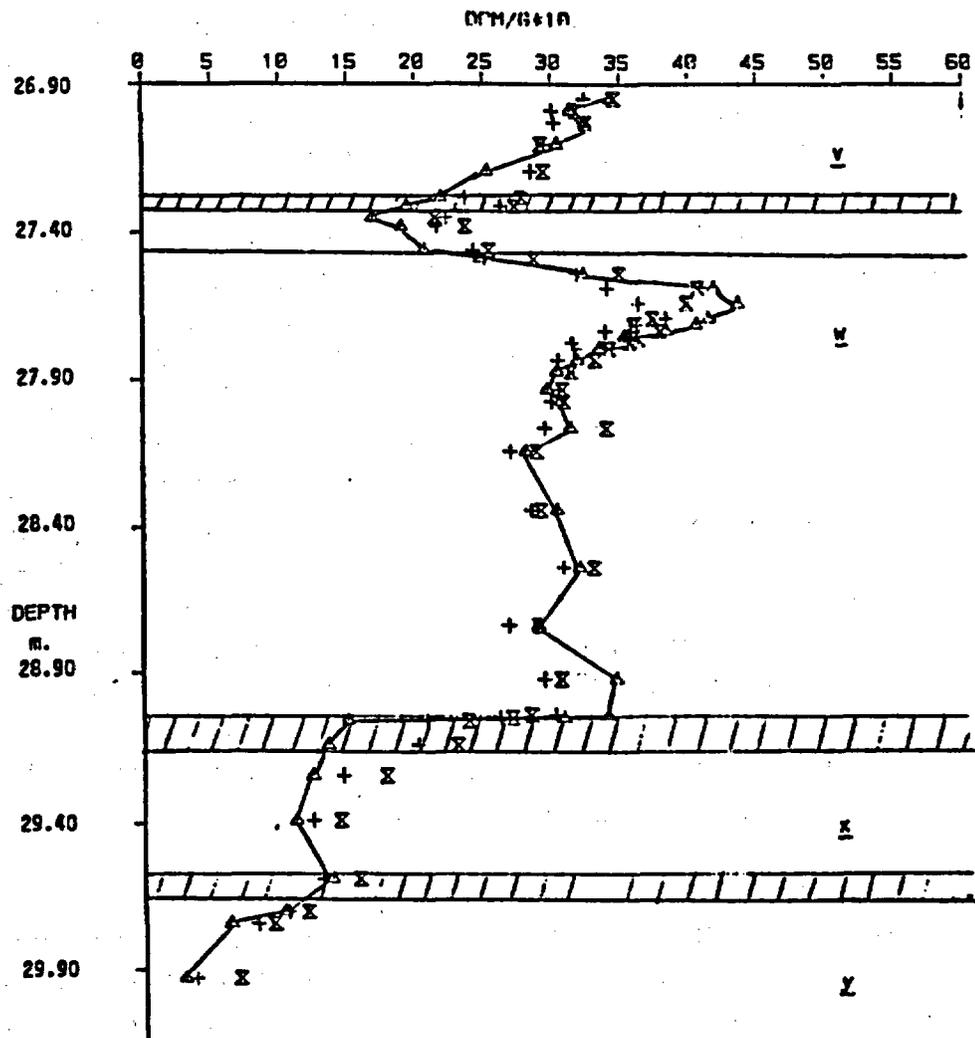


Figure 13. The same profile shown in Figure 12, for lower members of the ^{238}U chain, showing the departure from radiochemical closure for ^{226}Ra (bow-ties) and ^{210}Po (crosses). The profile and symbols for ^{230}Th are as used on the previous figure.



been immediately sorbed onto the sediments, since conditions have been mildly reducing and the mobile form, $^{234}\text{U}^{6+}$, would not be stable.

The effective diffusion coefficient for U of less than $10^{-16} \text{ m}^2/\text{s}$ reported previously has been supported in parallel studies by the same group on other piston-core material from the same area (Colley, et al, 1988, in press) where pore-water analytical data are available in addition to the solid phase radionuclide contents. The distribution of U between pore-water and sediment allowed the calculation of R_D values of between 300-1500 $\mu\text{g/g}$ (considering only the original authigenic mineral source of U prior to mobilisation) and between 900-15,000 for the total U present in the sediment. These values were considered low compared to the apparent immobility of U suggested by the radiochemical data from the solid phase alone, and described above. If the U peaks are assumed to have acted as sources for diffusive migration of U in solution, then for the 60,000 year age of this particular redox front peak, an effective diffusivity of $2 \cdot 10^{-15} \text{ m}^2/\text{s}$ would be required to explain the solid phase data. Multiplying this D_{eff} value by the R_D values obtained above produces a diffusivity in solution which can be compared to literature values. This (between 10^{-12} and $10^{-13} \text{ m}^2/\text{s}$) proved to be about two to three orders of magnitude lower than standard values, a feature that is taken as indicative of environments where organic complexation of U has occurred (Elderfield, 1981). Additional work on pore waters from the MD24 site produced some U concentrations in solution which were orders of magnitude lower than the predicted solubility of UO_2 or U_4O_9 , suggesting solubility control of U^{4+} by an adsorbed phase.

The evidence described, not only of the potential immobility of U-series radionuclides, but also of the mechanisms controlling the diffusivity and solubility of U species continues to provide useable data for performance assessment, and it is hoped that the final compilation of this interesting and diverse dataset will keep this application very much in mind.

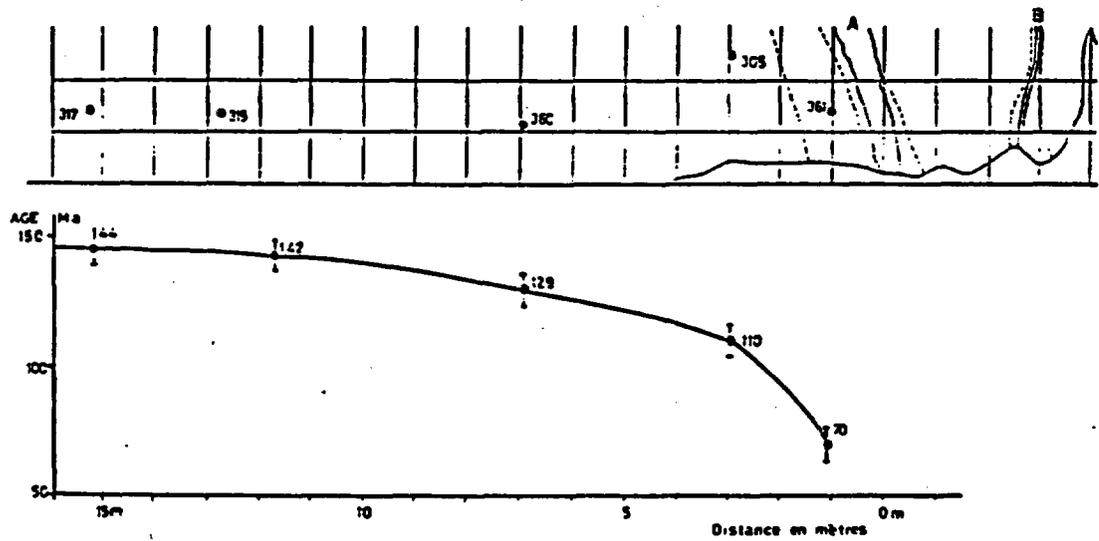
2.2 Transport processes in hard, fractured rocks

2.2.1. Elevated temperature migration in granitic rocks

The BRGM (Orléans) study (contract number 72) of trace element distributions and behaviour around a hydrothermal vein intruded into granite was completed this year (Piantone, 1988). The study, at Fombillou in the southern Massif Central, was formulated as an analogue of radionuclide retention processes which might occur if hot fluids which had been generated during passage of groundwaters through the near-field were to migrate along a fracture in the repository host rock. It might also be considered an analogue of alteration and diffusion processes in the rock of the very near-field immediately surrounding a waste container, in which case the mineralised vein could be regarded as the source of radionuclides for migration into the rock, rather than the trap for radionuclides in groundwaters passing along the fracture.

The vein was formed in a number of hydrothermal events, commencing with a first flux of low salinity fluids at temperatures of 300-480°C, followed by fluids of variable, but generally higher salinity at lower temperatures (110-140°C) which formed the core of the vein. The vein complex is enriched in W, Sn, U, K, B, Pb, As, Sb, Cu and Ba. The thermal impact of vein emplacement on the host rock was indicated by studies of fission-track annealing temperatures in apatite mineral grains. Figure 14 shows evidence of the thermal profile away from the vein, although it is thought that subsequent weathering of the system has smoothed this from an originally much sharper rise in the immediate vein contact zone. Geochemical evidence for the volume of rock affected by the vein emplacement shows that chemical exchange between rock and fluid phases has occurred to distances up to about 4.6m outwards from the vein. Beyond about 2.7m there is no apparent change in mineralogical properties. Significant alteration to the host rock was limited to a zone about 1.2m wide. For the transmissive fracture analogy, these figures represent much larger volumes of rock than might be affected by realistic fluxes/temperatures in a repository environment, but for the near-field (adjacent to canister) analogy the volumes of rock affected are probably very similar. The whole system has been subject to supergene (weathering) alteration and redistribution of elements, which leaves a secondary geochemical

Figure 14. Apparent relative ages of apatites derived from fission-track dating, as a function of distance from the main vein (A) at Fombillou. Although the shape of this curve has been affected by later weathering processes, it can be interpreted as a thermal profile showing the impact of vein emplacement on the rock.



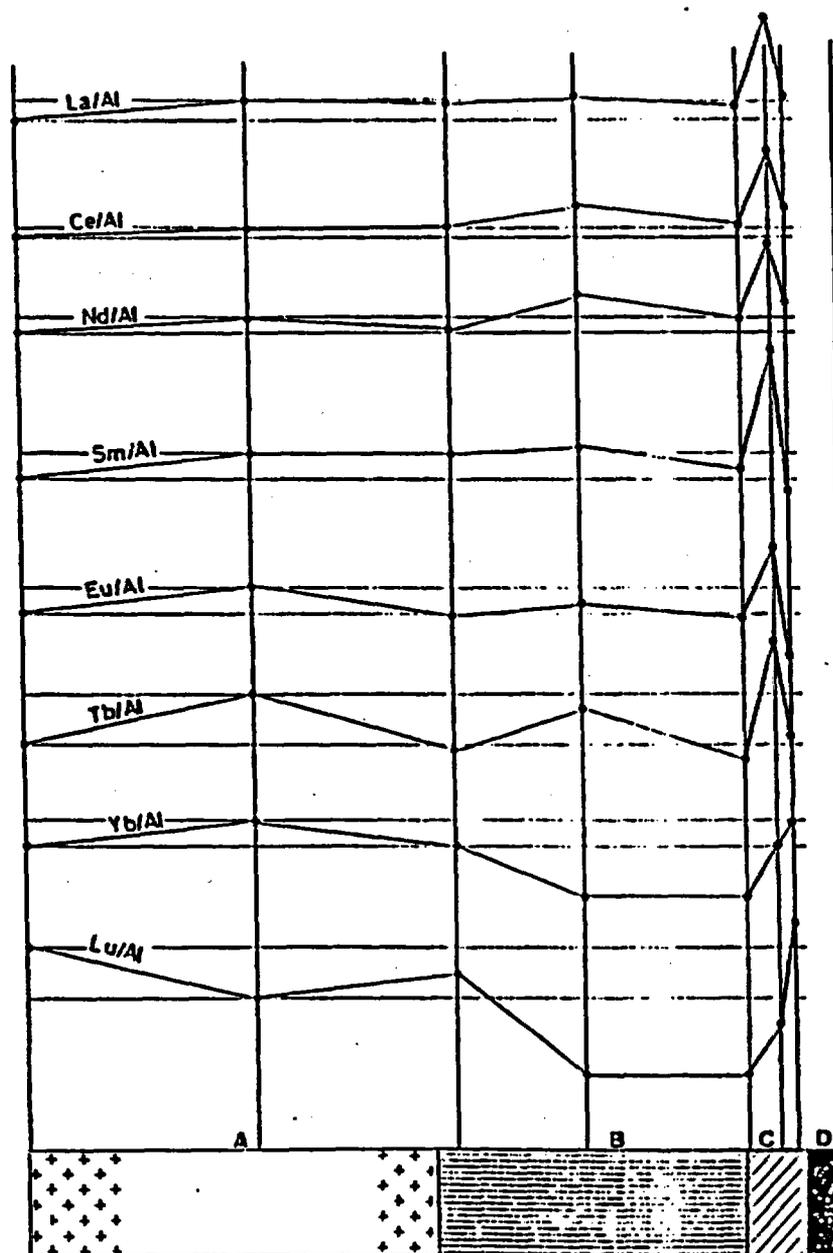
pattern overlain on the hydrothermal picture.

The hydrothermal alteration to the host rock which was associated with the vein emplacement took place under reducing conditions and resulted in the formation of an illite/smectite mineralogy out to about 0.5m, and an illite dominated mineralogy out to about 1.2m. Subsequent weathering at ambient temperatures has taken place in oxidising conditions, initially rather acidic, but later reaching equilibrium at a near neutral pH. During the formation of the illite/smectite alteration closest to the vein the mineralogy underwent a volume increase with a tendency to reduce porosity and block microfractures in the rock.

The mobility of trace elements during the hydrothermal events was controlled by the dissolution of primary minerals in the host-rock, and the rate of transport in by the warm fluids. It should be noted that these fluids were very depleted in CO_2 and consequently carbonate complexes have not been involved in any of the transfers now described. For example, Sr, which would normally have been fixed in calcite shows no sign of being retained within the system. Pb, Sb and Ti appear to be preferentially fixed by sulphides, sulphates and phosphates. The rare-earth elements (REE's) are enriched in the vein itself, and have been fixed in the clay minerals and newly-formed phosphate minerals away from the vein (Figure 15). In the illite/smectite zone both light and heavy REE's are enriched, while further out into the illite zone only the LREE's are enriched. This category includes Nd, considered to be the most appropriate analogue element for the trivalent actinides (Pu, Am, Cm). Eu appears to have been very mobile and has been effectively depleted throughout the system.

There are no data available from the site on the hydrothermal behaviour of uranium, although it is considered to have been introduced into the system during the earliest high temperature hydrothermal phase. As reported last year, the U-series disequilibrium studies show substantial remobilisation of uranium during weathering under oxidising conditions. Studies this year have shown the U to be fixed on iron oxy-hydroxides, principally the red coloured phase, lepidocrocite. The retention of U on such phases is strongly dependent on pH, and as noted earlier, the initially acidic conditions close to the vein (pH = 2, as indicated by the presence of jarosite) have not

Figure 15. Profiles of REE concentrations in the vein and host rock at Fombillou, normalised to the Al content of the specimens. A represents the unaltered host rock, B the illite zone, C the illite/smectite zone, and D the vein itself.



favoured U sorption, which is greater in the illite zone further away from the vein (pH about 7). The story is relatively simple, in that weathering has mobilised U from the host-rock (the vein has essentially not acted as a source of U for diffusion out into the rock), as evidenced by excess ^{230}Th in the rock, and both U and Ra have then been fixed in the clay rich zones near the vein. Th was slightly mobile during the hydrothermal period, but was fixed in phosphate minerals in the vein. It has remained immobile during weathering. Hf follows Th closely. These conclusions are summarised in Table 1, taken from Plantone (1988), which indicates the analogue applications of the conclusions of the study. Apart from the very interesting data on trace element and U-series behaviour, which support similar observations from other analogue studies, it is important to note the significance of phosphate minerals as potential actinide sorbents, and of phosphate complexes as actinide transporters. These observations provide very useful support to theoretical predictions from computer models.

The project involved a certain amount of geochemical modelling, for which the CEQCSY code was developed (Chemical EQUilibria in Complex SYstems). It is a basic thermodynamic equilibrium rock-fluid interaction model which uses the EQ3/6 database. No trace element modelling was performed, but the code was used to model the formation of illite during the hydrothermal alteration of the host rock. The principal finding was that in order to form the large quantities of illite found at Fombillou the system had to be hydraulically open, as the rate of illite formation depends on the rate of removal of water. In repository terms, this means that the development of substantial alteration haloes in the near-field depends on the openness of the fracture system. A tight hydraulic system will not favour illite formation.

The CEA (Fontenay-aux-Roses) study (contract number 149) of the uranium-rich vein at Jalerys in the northern Massif Central is in its second year, and differs from the BRGM study in that it aims principally at the second analogue concept described above; the vein simulating an elevated temperature source of radionuclides equivalent to a waste container. The vein under study is much richer in both natural series and REE's. A group of samples representing the vein, its clay selvage, and the host rock, has been obtained from a gallery at 170m depth in the mine. The sample site has subsequently been mined

Theme	Fossilium Site	Storage analogy
Subject studied	Metre-scale fracture and hydrothermalized wall rocks in granite.	Fracture of host rocks which may be affected by hydrothermal alteration in relation to the thermal period of waste.
Temperatures/ Eh/pH	Alteration I phyllite 100° & 200°C reducing environment Alteration II argillite 100°C reducing environment Alteration III supergene 25°C oxidizing/acid environment near drainage, then come into equilibrium with th. rock for a pH of about 7	Near field Near or far field
Variations of volume	Alteration I phyllite None Alteration II argillite Increase in volume of about 10 % for the most altered rocks Alteration III supergene Preferentially affects the altered zones, generating a secondary porosity.	Very weak effect on porosities of the environment where it develops except in fractures where newly-formed minerals may fill up the channelways through which fluids may move. Tendency to fill up fractures or rock pores, improvement of confinement.
Volume of rock affected by alteration	~ 1,20 m alteration discernible mineralogically ~ 2,70 m first perceptible geochemical variations	Probably much less than that affected by alteration at Fossilium, complex interlocked events
Major elements and constitutive trace elements	Mobility of these elements mainly controlled by dissolution of cardinal minerals and new formation of hydrothermal phases Phyllite alteration-gain in K Argillite alteration-gain in Fe No fixation of elements such as Sr. Absence of CO ₂ in the fluid allowing formation of Ca-carbonates. No substitution of Sr and Ca. Fixation of Th on the wall rock of the vein by low-saturation accessory minerals	Possibility of changing the physico-chemical nature of interstitial water by introduction of elements moved by the destabilization of original minerals No fixing of ⁹⁰ Sr at all but possible isotopic dilution with fluids derived from alteration of the host rock.
Trace elements	Pb, Sb Fixation of Pb and Sb by sulfides, sulfates and phosphates V Behaviour of V similar to that of Ti REE Fixation of REE in newly-formed minerals: phyllosilicates and phosphates. Incorporation of the REE in the lattice of hydrothermal phases and adsorption. General departure of Eu. U No data on its mobilization in hydrothermal environment except for introduction of U during the illite phase. In supergene oxidizing environment, U (VI) mobilization controlled mainly by iron oxyhydroxides which adsorb this element. Control of these processes by the pH of water. Th Th slightly mobile in hydrothermal environment, trapped by phosphates on the walls of the vein. Th immobile in supergene oxidizing environment. Rf Similar to Th.	Possible trapping of ²¹⁰ Pb and ¹²⁵ Sb by sulfides in reducing environment. Possible trapping of ²¹⁰ Pb by phosphates and sulfates in oxidizing environment. Possible retention of ²³⁸ Pa (III), ²⁴¹ Am et ²⁴⁴ Cm by similar mechanisms. But problems of competition, near the fixing sites, between these elements and REE released by alteration of the minerals of the host rock. Major role of phosphate. Non-retention of ²³⁸ Eu. Extreme mobility of ²³⁸ U in oxidizing environment but possible trapping by iron-oxyhydroxides Trapping of ²³² Th by phosphates and generally near immobility of Th. Rf: ²³⁸ U fission products which may occur in the waste

TABLE 1 : Analogies between the natural system and the storage site.

out. The sample profile extends for 30m from the vein into 'intact' granite host rock. An early phase of alteration at temperatures around 400°C affected the granite before the vein was emplaced. A second alteration phase was associated with substantial fracturing of the rock which allowed the vein to be formed from hydrothermal fluids entering the brecciated fracture at temperatures of 2-300°C. These slightly acidic fluids permeated the host rock and caused alteration of biotite to white mica for a distance up to 10m from their source in the vein. Further out the flux of fluids diminished and they progressively equilibrated with the rock, picking up Fe and Mg, becoming less acid, and altering biotite to chlorite instead of white mica. At the end of this episode the U mineralisation was emplaced along the same fracture in the form of pitchblende and sulphide minerals. Alteration of the host rock continued at lower temperature (100-180°C) in a period when further small-scale fracturing developed. These fractures are consequently filled with illite/smectite clays, which are also present throughout the inter- and intra-granular porosity of the granite, particularly in the 0-10m zone away from the vein. Finally, kaolinite and calcite have been formed in microfractures subsequent to the illite/smectite phase. Hematite formation was associated with each progressive phase of alteration.

The U/Th and REE's in the host rock are contained in phosphate, TiO_2 , and zircon minerals, and in pitchblende in the vein which, in the event, turned out to be rather poorer in concentration of Th and REE's than had been hoped for. The behaviour of these elements during the course of hydrothermal activity can be traced as follows:

1. During the higher temperature, vein emplacement phase the REE/U-Th host minerals were altered to release these elements. However, they were generally fixed again within a very short distance (mms), generally on secondary iron and titanium oxides (U), carbonates (REE's) or silicates (Th). Consequently diffusive migration of these elements was very limited.

2. During the low temperature period after vein emplacement uranium was mobilised from the vein itself rather than the host rock, but was again fixed, this time in the clay, oxide, and carbonate phases now filling much of the microporosity of the rock. Carbonate fixation is particularly important in the zones furthest out from the vein, while

clays dominate the near-field zone. The overall U contents of these minerals are rather low, at 15-30ppm.

A number of general observations can be made at this stage of the study. First it has been noted that diffusion of U into microfractures in mineral grains (matrix diffusion) has been less important than transport in small fissures. Second, there is again supporting evidence for the role of carbonates and oxides in retaining U, as well as clay minerals. Third, the very limited mobility of Th and, more unusually, REE's on the micrometric scale has been recorded. The work will proceed as data are gathered on the compositions of the hydrothermal fluids (from analysis of inclusions) and on more detailed modelling of the trace element distribution profiles only recently obtained. One objective posed in the previous report now seems unachievable: the thin (10-20cm) smectite selvage between the vein and the host rock turned out not to have acted as a barrier to fluid movement from the vein into the rock as it was formed progressively from the host rock during the vein emplacement. It will thus not be possible to model transport across it during the mineralisation phase. Consequently the study has become more an analysis of global mobilisation and retention of analogue elements rather than retention during migration along a specific pathway.

This latter problem is frequently being encountered in similar hydrothermal mobilisation studies both in the EC and elsewhere, as it is being found that the many superimposed phases of hydrothermal activity can make interpretation of trace element behaviour highly complex. Both the CEA and BRGM studies do, however, go a long way towards unravelling the fate and eventual sinks of trace elements in natural systems subject to varying temperatures and fluid fluxes over long periods.

2.2.2. Matrix diffusion in granitic rocks

The previous review on work in this area focussed on the diffusion modelling (UKAEA) used to explain anion profiles in blocks of granite which had been immersed in seawater (contract number 74). This project had been concluded prior to the review, and the issues it had raised were fully discussed at the plenary meeting in 1988. The review noted that a new contract (number 143) run by the

Universities of Exeter (UK) and Oviedo (Spain), then coming on stream, would effectively pick up the baton and address these issues. Essentially the issues concern the lack of an observational database on the distribution and nature of microporosity around fractures in granites which have undergone various stress and rock-fluid interaction histories. An additional problem is the effect of core extraction and subsequent sample handling on the porosity observed.

The authors of this programme (Heath, 1988; Rodriguez Rey and Heath, 1988) started by reviewing available literature and concluded that while matrix diffusion models often assume that the whole volume of rock is available for diffusion, observations of the amounts of rock affected by, for example, hydrothermal alteration adjacent to a vein, or iron-staining adjacent to weathered fractures suggest there may be some limit to the extent of diffusion. Additional evidence comes from measurements of U-series profiles away from fractures in granites, some of which indicate a practical limit of a few centimetres for diffusion into the matrix.

The main focus of sampling was originally intended to have been the IPES underground research laboratory at Aldeadavilla, but after suspension of this project sampling has concentrated elsewhere in Spain. Material has been collected from the Gondomar and Gallo granites at Pontevedra, Galicia, and from the El Escorial granite in Madrid. Additional material is available from the Stripa and Whiteshell URLs.

Digital image processing is being used to analyse optical and electron microscopic images of thin sections of granite. The method can be used to estimate factors such as the textural coefficient, which is a measure of the form and orientation of the granular mass, and the grain packing density. Some specimens are being impregnated with fluorescent resins at elevated pressure, but the effect of the technique on the porosity is not known. A novel technique using ultrasonics and known as scanning acoustic microscopy is being tested. The technique is capable of detecting very fine cracks which would not be seen with optical or electron microscopy. An alpha-spectrometry methodology for analysis of U-series equilibria in samples around fractures is being developed, and has been tested on

some of the samples from Stripa.

At the time of writing no detailed results were available, as the first year has been spent in assessing, testing, and developing a wide variety of techniques for measuring porosity and permeability, and for obtaining good U-series profiles. It is hoped that the second year of the project will see good returns from this preparatory and scoping work.

3. CONCLUSIONS AND PROSPECTS

The mid-point of a project is always a dangerous time to make firm predictions on the outcome of the work. However, a number of general trends are emerging which are worth commenting on:

1. The MIRAGE analogue programme is a microcosm of all the natural analogue programmes which are currently focussed within the CEC NAWG forum. It contains projects which vary from simple, but nonetheless interesting and useful qualitative observations, to rigorous attempts to validate aspects of specific geochemical models/codes used in performance assessment. In this sense it matches well the prediction made in last year's report, that analogue information will fulfill a variety of needs from the mildly confidence-building to the vital 'final test' of our ability to build realistic predictive models.
2. There is a strong indication that the various bits of MIRAGE are converging; models being developed are being tested on real systems, laboratory geochemical experiments and results are being tested or challenged by measurements from the natural world, and the databases being built are being assessed with a more enlightened understanding of processes in groundwaters. At the end of the programme it ought to be possible to sort and trim the laboratory data and focus the effort in areas such as the COCO exercise (see Research Area "Geochemistry of Actinides and Fission Products"), based on the way in which analogues and in-situ experiments have improved our knowledge of what are and are not valid mechanisms and parameter ranges for real (and appropriate) geochemical environments.

3. One of the preliminary findings of two of the analogue projects is that the state of the CHEMVAL database as used in PHREEQE (for example) justifies further work. This is a very positive result, and shows how, without proper control of models by natural systems, they could produce erroneous results if used 'blind' in performance assessment.

4. Despite much earlier interest in using surrogate elements as analogues for radionuclides in waste streams, almost all the analogue studies have now focussed on the natural U-series elements. Even the REEs are receiving only limited attention. The dominating importance of organics, phosphates, carbonates and oxy-hydroxides in controlling the solution speciation and sorption behaviour of uranium continues to be emphasised in all the projects.

5. The studies of hydrothermal processes highlight the ability of neo-formed minerals in the near-field of an elevated temperature HLW repository to fix radionuclides very locally to their source. However, the degree to which illitisation of the host-rock (or a bentonite buffer) is possible does seem to be very dependent on the hydraulic openness of the rock, which means that two potentially beneficial processes are counterposed.

6. There remains very considerable potential for additional studies of transport processes in clay-rich sediments, using the broad information base built up over the last few years for the Plio-Pleistocene clays of central Italy. It has not been possible to follow up all the features of interest which have been identified during the MIRAGE programme to date, and there is clearly scope for model testing and collaboration between a number of principal investigators in the CEC-sponsored programme.

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