ORNL/FTR--3535

**OAK RIDGE NATIONAL LABORATORY**

DE90 007487

OPERATED BY MARTIN MARIETTA ENERGY SYSTEMS, INC.
POST OFFICE BOX 2008, OAK RIDGE, TENNESSEE 37831-6285

# ORNL
# FOREIGN TRIP REPORT

ORNL/FTR-3535

DATE: February 22, 1990

SUBJECT: Report of Foreign Travel by John F. McCarthy, Research Staff Member, Environmental Sciences Division

TO: Alvin W. Trivelpiece

FROM: John F. McCarthy, Environmental Sciences Division

PURPOSE: To present a paper at the 10th meeting of the European Community's CoCo Club, at Harwell Laboratory, Oxford, England, and to visit subsurface field sites of the British Geological Survey, at Nottingham, United Kingdom.

SITES VISITED:

| | | |
|---|---|---|
| 2/1-3/1990 | Nottingham, United Kingdom | G. M. Williams |
| 2/4-8/1990 | Oxford, England | M. Ivanovich |

## ABSTRACT:

The primary purpose of this foreign travel was to attend the 10th meeting of the European Community's CoCo (colloids and complexation) Club to learn about research on groundwater colloids in Europe and inform the CoCo participants about the colloid subprogram of the U.S. Department of Energy (DOE) Subsurface Science Program. The goal of CoCo Club research, and of the umbrella MIRAGE (MIgration of RAdionuclides in the GEosphere) Project, is to develop data and understanding necessary to complete safety assessments for licensing nuclear repositories in Europe. The emphasis of CoCo Club research is sorption of radionuclides to organic and inorganic colloidal particles. The traveler also visited the British Geological Survey (BGS) headquarters and a BGS field site. Discussions focused on development of innovative drilling equipment for minimizing aquifer disturbance, development and application of computerized resistivity tomography for aquifer characterization, and laboratory research on the role of organic matter on metal transport. The trip was successful in that the traveler obtained a comprehensive overview of European research on groundwater colloids which will help improve and focus DOE's colloid subprogram, and the traveler learned about advances in specific areas that will contribute to his own DOE-funded project.

---

## INTRODUCTION

The traveler has been appointed as the coordinator of the Geophysical Transport Processes/Colloid Subprogram of the U.S. Department of Energy (DOE) Subsurface Science Program (SSP). The goal of research in the colloid subprogram is to elucidate the role of organic and inorganic colloidal particles on the subsurface transport of contaminants. The European Community (EC) has funded a large body of hydrogeochemical research for the last five years called the MIRAGE (MIgration of RAdionuclides in the GEosphere) Project; the goals of their research is to develop data and understanding necessary to complete safety assessments for licensing nuclear repositories in Europe. A working group of projects within the umbrella MIRAGE Project is the CoCo (colloids and complexation) Club, whose focus is the role of organic and inorganic colloids in radionuclide transport through groundwater. The traveler was invited by the EC to attend the 10th meeting of the CoCo Club to learn more about the research being sponsored by the EC in the area of groundwater colloids, and to inform the CoCo Club participants about the DOE SSP and about specific research being conducted in the traveler's DOE-sponsored colloid research. The traveler accepted the invitation to help fulfill his duties as subprogram coordinator in assuring that DOE's research objectives benefited from advances in European research; in focusing DOE research on problem areas that advance and extend, rather than duplicate, existing understanding; and in encouraging European participation in a planned DOE workshop on strategies to manipulate groundwater colloids for environmental restoration. The meeting agenda and list of participants are included at the end of this report.

While in England for the CoCo meeting, the traveler visited the headquarters of the British Geological Survey (BGS) and one of their field sites. BGS has a very active research program in contaminant transport, including consideration of colloid transport. BGS has developed a field site for tracer and colloid studies that is very similar to a field experiment being conducted in the traveler's research project, and a number of areas of mutual interest were discussed.

## SUMMARY OF WORK

### Trip to British Geological Survey, Nottingham, United Kingdom, February 1 and 3, 1990

The traveler visited the British Geological Survey (BGS) headquarters and had significant interactions with the following individuals: Goeff Williams, a hydrologist geologist at BGS; Jennifer Higgo, a geochemist; Barry Smith, another geochemist; and Peter Warwick, a nuclear chemist from Loughbrough University in Nottingham who works closely with BGS. There were three areas of overlap in our interests:

a. improved methodology for installation of wells in unconsolidated sand aquifers using techniques designed to minimize disturbance to the surrounding aquifer and thus minimize opportunities for production of colloidal particles during well installation,

b. a new technique being developed by BGS to characterize lithology and porosity of subsurface environments by use of computer-addressed resistivity probes to construct a three-dimensional resistivity tomograph of the aquifer during tracer tests, and

c. the effects of natural organic matter on the movement of radionuclide contaminants through porous media (sand column experiments).

## 1. Well Installation for Colloid Sampling

Goeff Williams and colleagues at BGS have fabricated and tested a new type of drill bit specifically designed for installing wells with minimum disturbance in unconsolidated aquifers for purposes of collecting colloidal samples. The drill bit is screened from the aquifer material by a collar that extends slightly below the drill and prevents drilling fluid or ground rock from entering the aquifer. Water is used as the drilling fluid but the fluid is prevented from entering the aquifer due to a plate across the bottom of the drill bit that deflects the water up a middle annulus so that the fluid does not enter the screened area outside the drill bore. The details of the design are described in a publication provided by BGS.

This improved drill design may be applicable at DOE SSP sites, especially field sites targeted for colloid studies. One of the great concerns of course in sampling colloids is that the installation of the well creates potential artifacts by disturbing the surrounding aquifer and introducing drilling mud and other colloidal materials into the formation. This self-drilling screened well prevents those complications by forcing the screened area of the well to be in direct contact with the formation while keeping the bit and the drilling fluid recessed behind a skirt that prevents the intrusion of the drilling fluid into the surrounding aquifer. Williams tested the exclusion of drilling muds into the aquifer by putting receptivity probes on the screened exterior of the well and confirmed that there was no intrusion of the drilling fluid outside the borehole. Several of these self-drilling screened bores have been installed on an aquifer that they are instrumenting for injection studies at Drigg near the Cellarfield Nuclear Reactor area. The drill bit and the technology that they developed are particularly designed to drill the rock and shell aggregates that are present in their formation. It is possible that a similar concept with somewhat simpler design could be devised for unconsolidated sand aquifers such as at the DOE/OHER colloid field site at Georgetown, South Carolina. At the present time, BGS is conducting studies on the movement of nickel and cobalt injected into the aquifer under a forced gradient hydrologic regime. The design of the experiment, the initial model calculations of metal speciation, and the predictions of the transport have been described in the publications the traveler received from BGS during his visit. The design of the tracer experiment is very similar to the array installed at the Georgetown, South Carolina, site. There is an injection and a withdrawal well 5 meters apart with multilevel sampling wells at intervals of 1.5 and 3 meters between the injection and withdrawal well. The multilevel sampling ports are sampled by BGS using a vacuum manifold. They stressed the importance of maintaining a very constant injection rate during tracer experiments and have taken pains to ensure accurate flow rates by using sophisticated flow values to control the rate of withdrawal and rate of injection in their aquifer.

## 2. Resistivity Tomography to Characterize Aquifers

A second area of mutual interest involved new approaches being developed at BGS for characterizing the subsurface environment. The technique uses arrays of electrodes deployed over the surface and vertically along probes (with electrodes spaced every 5 cm) to construct a three-dimensional tomograph of the resistivity of the aquifer. The concepts and theory of resistivity measurements are not new; what is unique in the BGS approach is that each of the three-dimensional arrays of electrodes is individually addressed by a computer circuit board. The computer is programmed to automatically select pairs of electrodes to place a current across and other pairs of electrodes to monitor changes in voltage. BGS is now testing the system using a chloride tracer injection (see information on the field site visited on February 8, 1990).

The BGS is now collecting data at a highly instrumented field site and hopes to use computer software to form a tomographic three-dimensional image of the resistivity profile in the groundwater. The traveler was particularly interested in the use of this technique for detailed characterization of the porosity and hydraulic conductivity of shallow aquifers; however, the resistivity tomography approach has a number of other potential applications. Resistivity of the subsurface environment can be affected by a number of factors including the degree of saturation, salinity of the water, porosity of the water, and nature of the mineral surfaces. The probes can, for example, be used to measure the storage capacity represented by the capillary fringe, or changes in saturation of the vadose zone during storm events.

Currently, resistivity tomography and interpretation of the data for characterization of the subsurface are still in a development stage. The computer software and electronics are developed, but the acquisition of the first data base of resistivity measurements was scheduled for the week of February 12, 1990. In addition to their own applications, BGS is collaborating with Dr. John Cherry at the University of Waterloo in a field experiment to follow a plume of organic solvent injected into the Borden site. BGS will attempt to monitor the development and migration of a three-dimensional plume of solvent based on changes in resistivity of the groundwater containing the solvent.

This resistivity approach appears to have a great deal of merit and would be particularly applicable for characterization of the DOE colloid field site at Georgetown, South Carolina. Preliminary data from analyses of cores and from results of chloride tracer tests have demonstrated that the site is characterized by complex changes in the chemistry, mineralogy, lithology, and hydrologic conductivity of different horizons.

Interpretation of the mobility of colloids in the planned injection experiment at the Georgetown site would be significantly improved if noninterventive measurement of resistivity profiles could provide more direct in situ evidence of the differences in porosity and hydraulic conductivity with depth. The traveler will monitor BGS's progress in testing and validating the resistivity tomography approach to assess whether the technique could contribute to experiments at the Georgetown site or at other DOE/OHER field sites.

## 3. Role of Natural Organic Matter in Transport of Radionuclides

The third area of interaction of the traveler with the BGS was with the geochemists, Jennifer Higgo and Barry Smith, and with Peter Warwick, a radionuclide chemist who is working in collaboration with BGS at Nottingham. The main thrust of the work at BGS in radionuclides deals with radionuclide migration through porous media. I was particularly interested in the sand column experiments they were conducting on the effect of natural organic matter on the mobility of radionuclides of nickel and cobalt. The experiments are, in many ways, analogous to the experiments that have been conducted by the traveler's project in Oak Ridge dealing with the effect of mobile organic matter on the migration of organic and inorganic contaminants. BGS work does not specifically address the mechanisms or extent of retention of the organic matter in the sand columns but rather focuses on semiempirical observations of the cotransport of organic matter (measured by UV spectrometry), and of the radionuclides. In general, they find that the presence of natural organic matter accelerates the movement of the radionuclides through the column, although the effect is more noticeable with cobalt than it is with nickel.

The methods they used to measure the complexation of the radionuclides with the organic matter were of particular interest. Several approaches are being evaluated at BGS to quantify binding of the metals to the organic matter. Primary emphasis is on size-exclusion principles using either Sephadex G-10 size-exclusion chromatography or high-pressure liquid chromatography using a Synchropak size-exclusion column. The general principle is that the high-molecular-weight organic matter–radionuclide complex would be excluded by the column matrix while the inorganic radionuclide would be retained. The interpretation of the results is somewhat complicated by an inorganic complex of intermediate molecular weight. Nevertheless, both procedures offer great promise and are similar to approaches used by Dr. Moulin (see below).

BGS researchers do not extract and purify the organic matter they use in their experiments; however, they do concentrate it by tenfold (to approximately 135 mg C/L) using rotary evaporation. They expressed concern that some low-molecular-weight volatile material capable of binding the radionuclides could be lost during the rotary evaporation. Their sand column experiments use natural material: the sand is from the aquifer at their Drigg field site, and the organic matter is concentrated from the groundwater at Drigg. The sand columns are run using a simple gravity flow system with fluid velocities that are much higher than in natural groundwater systems. Both BGS and the traveler (who has been using similar flow rates in his own experiments) have been considering methods for conducting experiments over long times at very slow flow rates. BGS is about to test a new flow control device that the traveler was not aware of that may be a very cost-effective and useful tool for this application. It is a commercial unit, manufactured in Massachusetts, that uses a gravity system with a electronically controlled flow regulator. The traveler received brochures on this apparatus and will consider its application in his DOE-funded project in order to make the flow rates during column experiments more similar to the natural groundwater flow rates at the Georgetown, South Carolina, site.

All in all, the visit to BGS was a very interesting, worthwhile, and informative journey. The interests and approaches used by the investigators at BGS closely parallel those being used in the investigator's own project. The hydrologic and geologic skills at BGS are very innovative and creative and may be useful in some aspects of the DOE SSP.

## CoCo Club Meeting, Harwell Laboratories, Oxfordshire, United Kingdom, February 4 - 8, 1990

The traveler attended the 10th meeting of the CoCo (colloids and complexation) Club of the European Community's MIRAGE (MIgration of RAdionuclides in GEosphere) project. The meeting was attended by approximately 40 investigators, most of whom were involved in projects funded by the MIRAGE project. Observers from non-European-Community countries were also present, including Sweden, Finland, and the United States (represented by the traveler). The structure of the meeting was a series of progress reports and discussions from individual project participants. A copy of the agenda is attached, and highlights of the individual presentations and subsequent discussions on the different research areas are described here. The agenda was divided into two components: the first dealt with characterization of colloidal organic matter and sorption of radionuclides to the organics, while the second topic focused on sorption of radionuclides to inorganic colloids.

### 1. Complexation with Organics

The first research area discussed was the complexation of radionuclides with natural organic matter. Dr. V. Moulin, of the French Atomic Energy Commission (CEA), reported on the isolation, characterization, and concentration of humic substances in groundwater at Fanauy-Augeres, a granitic formation being considered as a repository. Organic matter was isolated by DEAE-chromatography. Organic carbon levels were approximately 2.3 mg C/L with a pH of approximately 6. About 41% of the total organic carbon was humic substances, mostly fulvic material. Radiocarbon dating aged the fulvic acid at about 600 years old, whereas the humic acids component was more than 5000 years old. The ability of the organic matter to complex radionuclides was also studied using chromatographic separation (Sephadex G-15 size-exclusion columns) as well as spectroscopy to detect americium complexation, and laser-induced resonance spectroscopy to detect complexation of curium with humics. The complexing capacity of the Fanauy-Augeres was approximately the same as that of Gorleben waters (a German repository site). In these waters, as has been reported for other waters, there was an increase in the complexation capacity by the humics with increasing pH in the pH range 3 to 5. Comparison of the different techniques for measuring complexation was also discussed. The spectroscopic method requires higher concentrations of americium for detection and gives lower stability constants. In contrast, the fluorescent LIRS method can detect much lower concentrations of the curium–organic complex and yields higher stability constants. The higher stability constants estimated by the fluorescent method were attributed to the lower surface coverage that could be detected by that method and reflected sorption only on strong binding sites.

Dr. G. Buckau, Technical University of Munich, described the German component of an interlaboratory comparison of characterization of humics from the Fanauy-Augeres and Gorleben sites and commercial standard Aldrich humic acid. The intercomparison is a key element of the CoCo Club strategy to ensure the accuracy and consistency of results among participants throughout Europe. There was a discussion of techniques for determining the molecular size of the humic acids. Gel permeation chromatography (GPC) was used by Dr. Buckau, with size calibration based on retention of globular proteins. Two main peaks were observed with the GPC method: a very high molecular weight peak and a much broader lower molecular weight peak. The low-molecular-weight peak was similar in both the humic and fulvic acid components, whereas the high-molecular-weight peak was present in only the humic acid. Filtration was discussed as another method to determine molecular size of humics. It was noted that the Amicon molecular weight filters provide correct cutoffs based on retention of globular protein standards but generally measure a higher molecular weight range than the gel permeation chromatography. Results of the size distribution of humics was similar between sites, as was elemental composition of the organic matter. Functional group composition of the humic acids was determined using titration with barium hydroxide to get the total anion functional groups, while titration with calcium acetate was used to quantify the carboxyl functionalities, and the hydroxyl functionalities were determined by the difference between the two.

Mr. H. Wimmer, Technical University of Munich, discussed spectroscopic analysis of humic acid complexation of curium by using fluorescent approaches (LIRS). The binding of the humic acid causes a shift in the fluorescent spectrum of the curium from 594 nanometers to 601 nanometers. The complexation was also analyzed by using excitation spectra and fluorescent lifetime measurements to demonstrate and to probe the mechanisms of the curium–humic acid complex. All three spectroscopic methods indicated increased complexation of the curium with increasing humic acid concentration. Based on the spectral shifts, it was concluded that the humic acid bonding affects the transition state of the curium, suggesting that the humic acid forms an innersphere complex with the curium.

Dr. G. Bidoglio, Joint Research Center in Ispra, Italy, reported on the effect of major cations on the interactions of humic acid with radionuclides, using LIRS. There were two interesting aspects of this presentation. First, the major (nonradioactive) cations were demonstrated to have a large effect on the complexation of radionuclides such as europium by fulvic acid, presumably by a cation competition mechanism. Second, it was suggested that measurement of the binding of the radionuclides using the fluorescent method could be used to probe the interaction of major cations such as aluminum interacting with humic acids. The noninterventive nature of the LIRS method is a significant advantage of the technique, but a cation must have an absorption spectra to be directly probed by the system. Radionuclides such as americium and curium have a useful spectra, but Bidoglio suggests that the technique could be extended to studying nonfluorescent compounds such as aluminum by observing the effect of aluminum on the behavior of a fluorescent probe element such as americium or curium.

Dr. L. Carlson, Riso National Laboratory in Denmark, reported on a study to identify labile protons in humic acids by exchange of proton in deuterated water. He had hoped that this method could be used as an indicator of accessible binding sites within the humic molecule. Unfortunately, results were highly variable and did not correlate with measurement with functional groups. It was concluded that this was not a useful method for quantifying binding sites.

Dr. Peter Warwick of Loughbrough reported on the association of nickel with organic matter in a waste plume at the Villa Farm research site; nickel has been observed moving away from waste lagoons at this site. The groundwater was collected and filtered by size. Most of the nickel was associated with hydrophilic organic material, defined as the portion of the humic material not retained on a reverse-phase high pressure liquid chromatography column. Gel permeation chromatography indicated that the nickel co-chromatographed with the humic and fulvic acid peaks. Furthermore, laboratory studies using polarography also supported, in at least qualitative terms, the presence of the nickel-humic acid complex, with complex formation increasing dramatically in the pH range from 3.5 to 4. Interestingly, the kinetics of the association of either nickel or cobalt with organic matter was very slow, requiring 22 to 44 days to achieve equilibrium. This equilibration is considerably longer than has been reported in the literature and in the discussions in the CoCo Club.

Dr. P. Henrion from Belgium reported on the association of organic matter with Boom clay, which is a highly reducing clay deposit being considered as a waste disposal site in Belgium. He demonstrated that under reducing conditions, the iron-carbonate, siderite, may be an important component in the speciation of iron, and overall speciation may, therefore, be sensitive to the concentrations of calcium as calcium carbonate in the system. Boom clay has a very high organic content (about 1.9% organic matter). Dr. Henrion determined that the organic matter coating the clay appears the exclusive sink for the iron in the system, all of which is in the $Fe^{+2}$ form. Dr. Henrion speculates that the iron acts as a metal bridge between the clay surface and the organic matter. His evidence for this is that the treatment with acid liberates almost all the iron from the Boom clay and that subsequent increases in pH cause a release of almost all the organic matter. Treatment of base alone, without the pretreatment with acid to remove the iron, results in a loss of only about 5% of the organic matter in the clay.

Dr. Ewart's group at Harwell Laboratory reported on the binding of americium to organic matter in the field environment characteristic of cementitious waste disposal sites. The near field of a cementitious disposal site is characterized by a very high pH (pH 12), high calcium (about 0.001 M), with low carbonate and low redox potential. Under these conditions the actinide solubility is extremely low and the cementitious backfill provides a large degree of absorption capacity. In this environment, the organic matter appears to have an extremely small effect on solubility of the actinides, presumably because the relatively high concentrations of calcium cause precipitation of the organic matter. It was concluded that in the near field cementitious environment, there will be little enhancement of americium solubility and transport by humic acids due to precipitation of the humic acids by the calcium.

Dr. Jennifer Higgo of the British Geological Survey reported on the rates of diffusion of radioactive cobalt through porous media, with special reference to the effect of organic matter on the movement of the radionuclide. Dr. Higgo hypothesized that dissolved organic matter (DOM) is a mixture of solutes, some of which are capable of sorbing radionuclides, but which do not associate with the immobile matrix. Model calculations demonstrated, for example, that the retardation factor for a radionuclide can decrease theoretically by a factor of 10 if only 1% of the radionuclide is a complex of a DOM component with a retardation factor of 0 even though the remaining 99% of the radionuclide has a retardation factor greater than 5000. She presented data from diffusion experiments which are consistent with models indicating that the diffusion of americium is not controlled by the solubility of the americium or by the bulk migration of DOM in the solution; the data are more consistent with a model based on assumptions that a percentage of the radionuclide is associated with a minor DOM component having a very low retardation factor and the rest having a very high retardation factor.

To test this hypothesis, the BGS group is attempting to use radioactive iodine as a label covalently bound to natural DOM, using procedures that are typically applied to labeling proteins in biochemical research. Although the unreacted iodine did not behave in the diffusion experiments in a manner expected for an unreactive tracer (possibly due to bacterial fixation of iodide on the media), the radiolabeled, iodinated humic acid behaved as is typical for humic acids, based on detection of humic acid migration using UV absorbance.

Dr. G. Bidoglio discussed neptunium migration through granite. Granite columns were placed under high pressure, with equally high pressure applied to the outside of the column to create a strong seal between the column and the core of granitic material. Flow rates through the column were approximately 4 milliliters per day through the microporous structure of the granite. Dr. Bidoglio saw good breakthrough curves for tritium, technicium, and chloride (all nonreactive tracers), but no breakthrough of the neptunium. He also measured the breakthrough of natural DOM and observed a long, slow tailing breakthrough curve for the DOM; the organic matter that was able to move through the microporous structure of the granite was approximately 3 to 4 nanometers in size. In contrast to the experiments in the absence of DOM, the presence of DOM in the mobile phase resulted in breakthrough of neptunium from the column. However, only 10% neptunium was accounted for in the breakthrough curves, and the rest was retained on the column.

## 2. Basic Retention Mechanisms in Aquifer Systems

The second major topic for discussion involved studies directed at understanding the basic mechanisms responsible for retention of colloids in aquifer systems. John Ramsay from Harwell Laboratory in England made a presentation on collaborative work with Jean-Claude Petit from the Atomic Energy Agency in France on the use of Rutherford backscattering (RBS) as a technique for measuring the sorption of metals on mineral surfaces. Their work includes study of retention mechanisms of both natural and synthetic colloids on mineral surfaces (specifically amorphous and hydrated quartz, mica, and hematite). To a large extent, the work presented at the meeting was a demonstration of the ability of using RBS as a tool for noninterventively quantifying sorption on surfaces. The concentrations of the radionuclides on model colloids were much higher than would be relevant to an environmental situation. Nevertheless, they were able to demonstrate, for example, that they could detect cerium binding to colloids as a peak in the region associated with the wave number of cerium colloids. The shape of the peak for cerium bound to mica surfaces was different than that of the same cerium colloids bound to hydrated silica; the cerium peak was skewed in the latter example, possibly due to partial "sinking" of the cerium colloid into the gel-like surfaces of the hydrated silica. They also explored the effect of surface charge on colloid sorption to mineral surfaces. Negatively charged cerium colloids bound to silica in the pH range where the silica had a positive change; conversely, the cerium colloids did not bind to montmorillonite in the pH range in which the clay had a negative charge. In general, they found also that mineral oxide colloids, which are positively charged in the pH range of the study (pH 3-7), were strongly retained by quartz and mica, which have a negative charge. Furthermore, they calculated that the electrostatic interaction leads to very dense packing of the colloids on the surfaces. In contrast to the behavior of pure radionuclide colloids, "pseudocolloids" (i.e., radionuclide ions sorbed to a clay mineral or mineral oxide colloid) showed a low interaction potential because many of the mineral colloids have the same charge as the aquifer material and the charge repulsion prevents the association of the pseudocolloids with the mineral surfaces. The overall implication of this research is that the transport of radionuclides bound to mineral colloids may be of much greater significance to the transport of radionuclides than is the potential transport of true colloids, which are inherently unstable and have a high tendency to sorb and be retained by the aquifer. The discussion after this talk raised many issues concerning distinguishing mechanisms of absorption. Several participants raised objections that the very high concentrations of cerium used by the investigators prevented them from being able to distinguish precipitation versus true electrostatic interaction. In talks with the researchers at lunch, it was apparent that their goal at this stage of their research is more methodological than mechanistic; they would like to demonstrate and test the application of RBS for sorption studies. More recent research is applying the RBS technique to concentrations of radionuclides 3 orders of magnitude lower than the work that was presented.

Dr. V. Moulin reported on sorption of americium and neptunium on silica colloids. One part of her presentation was methodological comparison of the sorption of radionuclides to polyallomer versus polycarbonate tubes as a function of pH. The polyallomer tubes sorbed more radionuclides, but the sorption was insensitive to pH. Polycarbonate tubes had lower sorption at low pH, but the sorption increased dramatically at a pH greater than 5; by pH 7-8, sorption was significantly higher than that of the polyallomer tubes at the same pH. The second part of Dr. Moulin's presentation measured sorption of americium and neptunium to silica colloids, using ultracentrifugation to collect the silica colloids and quantify the sorbed radionuclides. Neptunium (thought to be +5 oxidation state) showed very little change of sorption with the pH, while the Am(III) showed increasing sorption onto the silica colloids as the pH increased between the range of 4 and 8. Mr. Heinrith (from Technical University of Munich, TUM) suggested that the lack of effective pH on neptunium sorption may be due to the fact that the researchers left their experiment open to the atmosphere, permitting the introduction of $CO_2$ into the sample. Neptunium, it was suggested, could speciate into the carbonate form, which would be negatively charged and show a decreased sorption at higher pH. In contrast, the americium was hydrolyzed to a positively charged form as the pH increased, thus explaining increased sorption as pH increased.

The discussion of Dr. Moulin's talk was followed by a presentation by Mr. Heinrith, who discussed his data on the effect of pH and $CO_2$ on the solubility of neptunium. Mr. Heinrith demonstrated that under atmospheric conditions, carbonate complexes can affect the speciation and sorption of neptunium. Speciation of neptunium to carbonate complexes was observed as spectroscopic shifts in the absorption of the neptunium at about 990 nanometers. Mr. Heinrith also noted a minimum in solubility of neptunium at about pH 6 or 7 due to the formation of neutral neptunium oxyhydroxide species, with positively charged neptunium oxide being the increasingly predominant species at lower pH, and negatively charged neptunium oxyhydroxide predominant at higher pH. Presence of carbonate also affects the solubility of neptunium at low partial pressures of $CO_2$. Positively charged neptunium oxide was the predominant species at low partial pressures, while at higher $CO_2$ partial pressure (including normal atmospheric concentrations), negatively charged neptunium carbonate complexes predominated. These observations supported his interpretation of Dr. Moulin's data on the apparent insensitivity of neptunium sorption to pH.

Dr. Wolfrum and Dr. Lang from GSF Institut für Hydrologie in Munich, West Germany, discussed intercomparison of different methods of laboratory tests for measuring sorption. A portion of the discussion was theoretical and a portion was a presentation of results comparing measurement of sorption using batch methods, column methods, and diffusion methods. This work was still in progress, and the presentation was limited to a general comparison of the different techniques. They pointed out that batch sorption measurements can be influenced by factors such as the concentration of the chemical and the volume-to-mass ratio of the solid phase. Column experiments can be affected by the flow velocity through the column, the length of the column, and by the shape of the breakthrough curve. Diffusion methods measuring sorption are sensitive to the complex sorption effects versus chemical effects such as speciation, which are not always easily described. In batch studies, the parameters can be controlled very simply, but volume-to-mass ratio is too high and the separation of phases may be incomplete. Column experiments have the advantage of having realistic conditions for physical transport but suffer from problems from unjustified assumptions of equilibrium. Furthermore, the solute concentration is changing across the column, and the geological medium is aging over the course of the column run. Diffusion incorporates processes of both diffusion and absorption, but the diffusion mechanisms are dependent on size, charge, and other factors. The conclusion was that each of the systems is self-consistent but that the differences between the different methodologies reflect differences in the initial conditions and boundary conditions, making it very hard to compare different methodologies on a quantitative basis.

Dr. Kim reported results of experiments on the speciation of americium under natural conditions and under conditions of changing redox and $CO_2$ concentrations. He used sediments and water taken from sites in the Gorleben aquifer. The Gorleben aquifer is anoxic, with approximately 1% $CO_2$. His experiments compared this condition with two modifications: in the first, oxygen was introduced, but $CO_2$ concentrations were decreased to 0.35% (atmospheric); the second modification also used oxic conditions but contained no $CO_2$. They determined the speciation of americium added to each of the systems by using laser photoacoustic spectroscopy (LPAS). The decrease in $CO_2$ and the increase in the oxygen resulted in a decrease in total americium complexes but an increase in americium humic acid complexes. The absence of oxic conditions and the absence of $CO_2$ decreased the total number of complexes but increased the amount of americium in ionic form.

In general, the experimental results agreed with speciation models such as MINEQL, except that the MINEQL model does not include consideration of the humic acid complex which was experimentally detected by the LPAS methodology.

In the final presentation in this session, Dr. Bidoglio from Italy compared different models for absorption with experimental data. Models he considered were constant capacitance models, diffuse layer models, and triple layer models, using data on the sorption of neptunium and plutonium on aluminum oxide surfaces. Preliminary results indicated a good fit between the observed sorption of neptunium on the aluminum oxide and modeling of the surfaces using a constant capacitance model.

### 3. Studies on Groundwater Colloids

There was a joint report from the TUM and Harwell Laboratories on characterization of the Gorleben site in Germany. Dr. Delakowitz (TUM) spoke first and reported that most natural actinides and lanthanides in the Gorleben aquifer were found associated with the dissolved organic matter in the size range of 1.5 to 30 nanometers based on size filtration. Cations such as Sr, Mg, Mn, and Ca are not adsorbed by humics. In the Gorleben aquifer, the largest numbers of colloidal particles are in the small size range (1.5 to 30 nanometers), and more than 99% of all the particles are in a size range of less than 100 nanometers; the greatest mass of colloidal particles is also present in the very small size range. Dr. Dearlove from Harwell reported on an independent set of analyses on the same aquifer; the results were consistent with Dr. Delakowitz's results. The Harwell group used Amicon hollow fiber filters, whereas the TUM group used Nucleopore membrane filters. The Harwell group concentrated on uranium and thorium series disequilibrium measurements. They demonstrated that, as with the actinides, most of uranium and thorium is adsorbed to colloids in the 1.5- to 3.0-nanometer size range (determined by size fractionation in the field under nitrogen and 1% $CO_2$ environment). In the Gorleben aquifer, more than 80% of the natural uranium is associated with colloids, and virtually all the thorium is colloid associated. The most interesting result was that the uranium and thorium series disequilibrium ratios indicated that the colloids were not in equilibrium with the groundwater. For both uranium and thorium there was a 50% discrepancy between most isotope disequilibrium ratios between the radionuclides in the ultrafiltrate (in solution) versus the uranium and thorium associated with the colloid fraction. Although not reported at this meeting, in previous discussions the Harwell group and others studying uranium isotope disequilibrium in natural uranium deposits have also reported the lack of equilibration between the colloid phase and the groundwater phase.

This concluded the presentations of the progress reports from participants in the CoCo Club.

## 4. CHEMVAL Computer Model Validation Program

There was another presentation by Dr. Timothy Broyd from SW Adkins in Oxford, United Kingdom, on the CHEMVAL Project, which focuses on validation of chemical speciation models, assessment codes, and data bases for safety assessment. Dr. Broyd reviewed the CHEMVAL program and how it interacts with the CoCo Club. The objectives of the CHEMVAL exercise are to verify and validate chemical speciation codes, verify and validate the coupling of those codes, and review and extend the thermodynamic data bases. Several activities are being conducted within the CHEMVAL project, including application of speciation codes to cementitious waters and validation of the codes by using both laboratory experiments and field observations. They are also verifying the codes by formulating a text case and conducting blind simulations at a number of laboratories. One of the activities that should be of general interest is the assembly and review of thermodynamic data bases. By January 1991, they should have completed a data base containing more than 675 aqueous species and several hundred solid species. The data base will be in DBASE-III format and will also include comments on the source of data and notes on specifics of each datum.

## 5. Traveler's Presentation to the CoCo Club

The traveler was allotted 35 minutes for an invited presentation on colloid research sponsored by DOE. The outline of the presentation follows.

1. Description of DOE SSP (scope, goals, motivation, subprogram organization) and a description of the colloid subprogram. This overview took about 5-8 minutes.
2. Scientific seminar on the traveler's DOE-sponsored research on chemical and hydrologic mechanisms controlling colloid mobility. To provide the CoCo participants an overview of the scope and the direction of research, three topics were presented:
   (a) Laboratory and field studies on mechanisms of organic colloid sorption to subsoils. This was data that has been recently published or is in press.
   (b) Co-transport of contaminants with mobile organic colloids in soil columns. This was recent research being prepared for publication.
   (c) Field studies in progress involving injection of organic colloids into a sand aquifer to elucidate mechanisms and extent of organic colloid transport.

There was a great deal of interest in DOE's program and in the scientific presentation. The traveler received a dozen requests for reprints and for additional information about our research.

## 6. Future CoCo Activities

MIRAGE is entering a new five-year phase of research and is soliciting new proposals. The goals and objectives of the new phase seemed quite similar to, and a logical extension of, the preceding five years of research. Although some in situ field experimentation appears to be planned, the predominant thrust of CoCo research is clearly laboratory oriented, and focused almost exclusively on chemical sorption of radionuclides to colloids. There is little if any consideration of the mobility of the organic and inorganic colloids themselves. It will take approximately nine months to solicit, select, and fund the new phase of research in MIRAGE (including CoCo).

## Summary of Traveler's Impressions about the CoCo Club: Relevance to DOE's Colloid Subprogram

In general, the traveler was very favorably impressed by the scientific quality of the presentations and the close coordination and collaboration among participants from different countries. While some of the collaborations are "shotgun marriages" imposed by the funding source, it is apparent that the frequent meetings (twice a year) have fostered genuine and very effective and productive collaborations among many of the investigators. DOE subprograms may wish to consider informal progress meetings at regular intervals to promote communication and foster interactions and collaborations among subprogram investigators.

The DOE colloid subprogram can benefit from research conducted by the CoCo Club. The CoCo participants have done an excellent job of developing and validating methods for sampling and characterizing groundwater colloids, which is one of the major needs in colloid research. They have just published an interlaboratory comparison of colloid characterization, which the traveler received. In addition, they have accumulated a great deal of information on sorption of radionuclides to organic and inorganic colloids (although much of that data is not available in the open literature). Funding priorities in DOE colloid research should include consideration of data and understanding already developed within the European program on radionuclide-colloid interactions. It should be noted, however, that CoCo research focuses on geological materials from European repository sites, and much of the research is semiempirical (specific to sites or to geochemical conditions at those sites) rather than mechanistic and thus more easily extrapolated to novel situations (such as might pertain at DOE sites).

The most serious criticism of CoCo research is their failure to consider processes of colloid transport. The DOE Colloid Subprogram Research Strategy has identified this problem as one of the most significant and least understood areas of colloid research, and places priority on this problem. Attendance at the CoCo meeting confirmed in the traveler's mind that this is a significant problem area where DOE research needs to contribute to fundamental understanding since no comparable research is being funded in Europe.

## Field Trip to BGS Field Site in Wallingford, February 8, 1990

The traveler and other interested CoCo Club participants visited the BGS Field Station at Wallingford (approximately 5 kilometers from Harwell Laboratory) to observe preparations for a tracer experiment designed to provide data for validating the resistivity tomography technique. Their experiment consisted of a central screened borehole for injection of tracer, and an array of multilevel sampling wells and resistivity probes radiating at 120° angles from the central borehole at 1- and 2-meter radii. The traveler was treated to a very informative day of discussions about the very practical aspects of installing wells and conducting in situ tracer tests that will greatly benefit his own research.

## APPENDIX A

## DRAFT AGENDA FOR THE TENTH MEETING OF THE COCO CLUB
## MONDAY 5TH FEB, 1990

08.30 Buses leave Hotel for Harwell.

09.30 1. Welcoming Address

2. Approval of Draft Agenda

3. Approval of the minutes of the ninth meeting of the COCO Club, Interlaken. 11th to 15th September 1989.

10.00 4. Complexation with Organics:- Report by participant laboratories. (Moderator J.I. Kim)

4.1 Interlaboratory comparison exercise on natural organics.

° Characterisation of site specific humic acids.
° Complexation with site specific humic acid and reference commercial humic acid.

10.45 Coffee

11.00 4.2 Other site specific natural organic, humic or fulvic compounds:

° Separation and characterisation.
° Complexation behaviour.

4.3 Complexation with man-made organics.

12.30 Lunch (Provided at Harwell).

13.30 4.4 Discussion

14.00 5. Basic Retention Mechanisms in aquifer systems. Report by participant laboratories. (Moderator to be announced).

5.1 Influence of natural organics and colloid generation on solubility, sorption and diffusion processes.

15.00 Coffee

15.30 Continuation of 5.1 and discussion.

17.00 End of Session.

APPENDIX A (Continued)

## TUESDAY 6TH FEBRUARY 1990

| | |
|---|---|
| **08.30** | Buses leave hotel for Harwell. |
| **09.30** | 5. Basic Retention Mechanisms in Aquifer Systems.<br>5.2 General Information on Mechanisms in Sorption Experiments. |
| **10.30** | Coffee |
| **10.45** | Continuation of 5.2 and discussion. |
| **12.30** | Lunch (Provided at Harwell) |
| **14.00** | Laboratory visits at Harwell.<br>Visit to 3 locations. Participants in 3 groups |
| **17.00** | End of Laboratory visits. |
| **20.00** approx | Dinner (Hosted by Harwell). |

APPENDIX A (Continued)

## WEDNESDAY, 7TH FEBRUARY 1990

| | |
|---|---|
| **08.30** | Buses leave hotel for Harwell. |
| **09.30** | 6. Studies on Groundwater colloids.<br>Report by Participant laboratories (Moderator. A. Avogadro). |
| | 6.1 Interlaboratory Comparison Exercises. |
| | 6.2 Generation Mechanisms. |
| **10.30** | <u>Coffee</u> |
| **10.45** | 6.3 Discussion. |
| **11.10** | 7. Contribution from Mr J. McCarthy. Oak Ridge Nat. Laboratory. |
| **11.35** | 8. Progress in the CHEMVAL project. |
| **11.55** | 9. Comment on the progress towards the 1990-1994 C.E.C. research programme. |
| **12.10** | <u>Lunch</u> (Provided at Harwell) |
| **13.10** | 10. Constructive discussion on future activities of the COCO Club. |
| **15.45** | 11. Miscellaneous. |
| **16.00** | End of meeting - Coffee before departure. |

## APPENDIX B

## 10th CoCo Club Meeting - Harwell - 5-7 February 1990

### Participants

| | | |
|---|---|---|
| Bert<br>Mr. B. Allard | University of Linkoping | Linkoping, Sweden |
| Mr. J. Astudillo | ENRESA | Madrid, Spain |
| Giovanni<br>Mr. G. Bidoglio | CEC - Joint Research Centre | Ispra, Italy |
| Mr. M. d'Alessandro | " " " | Italy |
| Bernard<br>Mr. B. Come | " " " | Brussels |
| Mr. A. Billon | CEA CEN-FAR | Fontenay, France |
| Valerie<br>Mrs. V. Moulin | " " | " " |
| Marco<br>Mr. M. Caceci | " " | " " |
| Jean-Claude<br>Mr. J.C. Petit | " " | " " |
| Gunnar<br>Mr. G. Buckau | Technische Universitat Munchen | Munchen, Germany |
| Mr. J. I. Kim | " " " | " " |
| Mr. B. Delakowitz | " " " | " " |
| Mr. H. Wimmer | " " " | " " |
| Mr. G. Heinrith | " " " | " " |
| Lars<br>Mr. L. Carlsen | Riso National Laboratory | Roskilde, Denmark |
| Goeff<br>Mr. G. Williams | BGS | Keyworth (UK) |
| Jenny<br>Ms. J. Higgo | " | " " |
| Barry<br>Mr. B. Smith | " | " " |
| Eberhart<br>Dr. E. Falck | " | " " |
| Mr. S. J. Williams | Harwell Laboratory | Harwell (UK) |
| Dr. M. Ivanovich | " " | " |
| Dr. G. Longworth | " " | " |
| Jeremy<br>Dr. J.P.L. Dearlove | " " | " |
| Mr. J.D.F. Ramsay | " " | " |
| Lorrie<br>Dr. L.R. Fellingham | " " | " |

APPENDIX B (Continued)

| | | |
|---|---|---|
| Peter<br>Mr. P. Fritz | GSF - Institut fur Hydrologie | Munich, Germany |
| Mrs. C. Wolfrum | " " " | " " |
| Mr. H. Lang | " " " | " " |
| Mr. P. Henrion | CEN/SCK | MOL - Belgium |
| Dr. A. Scholtis | NAGRA | Switzerland |
| John<br>Mr. J. McNaughton | WS Atkins Engineering Sciences | Epsom (UK) |
| Dr. T. W. Broyd | " " " | " " |
| Dr. D. Read | " " " | " " |
| Mr. M.M. Askariah | Imperial College | London (UK) |
| Mr. P. Rivas Romero | CIEMAT | Madrid, Spain |
| Mrs. U. Vuorinen | Technical Research Centre Finland | Espoo, Finland |
| Peter<br>Mr. P. Warwick | Loughborough University | UK |
| Dr. K. Butter | DOE | UK |
| Dr. J. McCarthy | Oak Ridge National Laboratory | Oak Ridge, TN (USA) |

# APPENDIX C

## ITINERARY

| | |
|---|---|
| January 31, 1990 | Travel to Nottingham, United Kingdom |
| February 1-3, 1990 | Site visit at the British Geological Survey |
| February 4-8, 1990 | Present paper at 10th Co-Co Club meeting, Harwell Laboratory, Oxford, England |
| February 9, 1990 | Travel to Knoxville, Tennessee |