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INTERNATIONAL SERIES OF INTERACTIVE SEMINARS

SUMMARY REPORT

MOBILITY OF COLLOIDAL PARTICLES IN THE SUBSURFACE: CHEMISTRY AND HYDROLOGY OF COLLOID-AQUIFER INTERACTIONS

MANTEO, NORTH CAROLINA

OCTOBER 4-6, 1988

Organized and Hosted by

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SEMINAR SERIES

U.S. DEPARTMENT OF ENERGY
SUBSURFACE SCIENCE PROGRAM

The International Series of Interactive Seminars (ISIS) have been organized to focus attention on scientific questions of importance to the Subsurface Science Program of the U.S. Department of Energy (DOE). The objectives of the seminars and the number of participants vary, but each seminar has common features that facilitate information exchange and a sharper definition of research questions.

Core participants are drawn from the academic, government, national laboratory, and international research communities. Each is a senior specialist in specific field. Approximately 80 percent of core participants are from scientific disciplines that are relevant to the seminar; others are consciously selected from outside these core disciplines in such fields as mathematics, numerical modeling, and other scientific areas. This format encourages challenges to accepted scientific wisdom on a given problem.

Advanced notices about the seminars are distributed to scientists who have requested to be kept informed about DOE research activities in subsurface systems.

ISIS programs are organized using a detailed agenda that focuses on key subtopical areas of importance to the program. The agenda ensures that nearly equal time is given to formal presentations and to discussion. Visitors can participate substantively during discussion periods by informal presentations or questions. Brief reports on the technical results of each seminar are prepared by the organizers. These working papers are available through DOE's Technical Information Center or NTIS.

Up to three seminars are organized annually. Initiative from outside DOE will be incorporated into the seminar series if accompanied by a willingness to host the seminar.

Meeting and travel costs are borne by host and participants. Further information may be obtained from Dr. Frank J. Wobber, Office of Energy Research (301-353-5549).

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ABSTRACT OF THE MEETING

A meeting on "Mobility of Colloidal Particles in the Subsurface: Chemistry and Hydrology of Colloid-Aquifer Interactions" was held on October 4-6, 1989, in Manteo, North Carolina. The meeting was part of the series of International Series of Interactive Seminars organized by the Subsurface Science Program of the Ecological Research Division, Office of Health and Environmental Research of the U.S. Department of Energy.

The purpose of the meeting was to examine the chemical and hydrologic factors controlling the transport and deposition of organic and inorganic colloidal particles in subsurface environments. Sessions dealt with technical difficulties in sampling and characterizing colloidal particles in groundwater, and with observations of colloid movement in laboratory and field systems, with an emphasis on the chemical and hydrological factors controlling transport. Discussion sessions attempted to summarize the concensus of the group on two important issues: (1) identifying natural conditions that promote either the transport or the deposition of colloids, with the intent of focusing attention on those subsurface environments with the greatest probability for the occurrence of mobile colloids, and (2) exploring strategies to manipulate colloid mobilization and deposition within subsurface systems to aid in remediation or mitigation of contamination at hazardous waste sites.

Participants includes senior researchers from from government research facilities and academic institutions in the United States, Canada, Germany, Switzerland, Sweden, and the United Kingdom. The primary problem in evaluating the significane of colloidal particles on contaminant transport centers on uncertainities in methods for sampling and characterizing groundwater colloids. While a number of valuable and innovative techniques were described, including a recent interlaboratory comparison of sampling and characterization methods, there still is no consensus on how well these methods reflect the true status of mobile colloidal particles that exist within natural groundwater systems. Several field studies provided strong evidence that colloidal particles do exist and are capable of transporting contaminants. Particularly strong evidence of colloid mobility is available for transport of biocolloids such as bacteria and viruses.

Based on the presentations and discussions, participants attempted to reach a concensus on the priorities for research on groundwater colloids. Highest priority was given to colloid sampling methods, understanding of the hydrogeochemistry of colloid formation and deposition, and application of this understanding to waste management. Important and critical laboratory studies must be tied to experimental questions driven by field studies, including comparative studies at a network of field sites that bound the range of conditions where colloids may occur. The document summarizing the meeting includes abstracts of technical presentations, summaries of discussion topics, and a description of research priorities.

INTRODUCTION AND SCOPE OF THE MEETING

This meeting was organized as a part of the continuing program of International Series of Interactive Seminars (ISIS) organized to help review and provide interdisciplinary guidance to the Subsurface Science Program of the U.S. Department of Energy (DOE). DOE faces numerous problems related to subsurface contamination which are long term in duration. Waste management programs are in progress to modify and to reduce hazardous and mixed waste streams and to control contamination from past waste disposal practices. The Office of Energy Research has Departmental responsibility for basic research and initiated a Site-Directed Subsurface Environmental Research Program (1) 1988. This initiative, combined with DOE's Subsurface Transport Program that has been underway since 1983, is now the Department's principal fundamental research activity related to contaminant transport in subsoils and in groundwater. This collective Subsurface Science Program includes research in hydrogeology, geochemistry, deep microbiology and other scientific disciplines. The significance of colloids in accelerating the transport of contaminants at DOE sites was identified early in 1982 as part of the planning process for DOE's Subsurface Science Program. In 1986, Oak Ridge National Laboratory and DOE organized a seminar on "Transport of Contaminants in the Subsurface: The Role of Organic and Inorganic Colloidal Particles" (2). The meeting reviewed current knowledge about the role of colloids on contaminant mobility, with an emphasis on the association of organic, metal, and radionuclide contaminants with organic and inorganic colloids. In the course of that meeting it became obvious that sampling and characterization of groundwater colloids was a major difficulty in describing the occurrence and abundance of colloids, and that there was a great need for a better understanding of the chemical and hydrologic factors that control the transport of colloidal particles in porous media.

Another meeting was organized at Manteo in 1989 to address those issues, and the summary of that meeting is reported here. The meeting summarized in this document brought together scientific experts from government research facilities and academic institutions in the United States, Canada, Germany, Switzerland, Sweden, and the United Kingdom to discuss scientific issues related to the sampling and characterization of colloids, and the chemistry and hydrology of colloid-aquifer interactions.

Dr. Frank Wobber, Program Manager for DOE's Subsurface Science Program, opened the meeting with a request to participants to review a DOE Colloid Subprogram Research Plan for fundamental research on the role of colloids in contaminant transport and remediation of contamination in subsoils and in groundwater (3). He pointed out that the Subsurface Science Program places a high priority on developing research plans and periodically evaluating future directions. Research program and subprogram documents are prepared by the Program Manager in cooperation with a research coordinator who assists DOE in setting a general research strategy for the subprogram, in selecting field research sites where interdisciplinary research is conducted, and in generally coordinating the subprogram. Program and subprogram scientific plans provide guidance to scientists who are interested in participating in DOE's research program. Key scientific issues addressed in these plans are reviewed at ISIS meetings such as this.

Dr. Wobber outlined DOE's Subsurface Science Program, and the Department's interest in long term, mechanistic research in subsurface sediments and ground water. The Department faces long term problems in cleaning up contamination at DOE sites; the costs of cleaning up dispersed contaminants over large areas and at many DOE sites are a major challenge in the next few decades.

New scientific approaches for remedial action can result from research that elucidates the chemical, physical and biological properties and processes that interact in the unsaturated zone and in ground water. He pointed out that research in mineral and organic colloids is illustrative of both a problem and an opportunity. Predicting the risk of contaminant movement implies fundamental understanding of the origin, hydraulics and surface chemistry of colloids; this has been emphasized in most published literature on the subject. However, DOE's research strategy (as reflected in the Site-Directed Subsurface Environmental Initiative (1) and Colloid Subprogram Plan) also includes attention to the opportunities of exploiting colloids to assist in contaminant stabilization or cleanup. For example, DOE sees that colloids might complement engineered methods, e.g. the manipulation of groundwater chemistry which encourages colloid formation. There may be instances when colloids could serve as contaminant scavengers and therefore vehicles to facilitate pump and treat decontamination. Taking a long range view of such basic research should be a part of Session III that will deal with strategies to manipulate colloids for waste management and environmental restoration.

Copies of the Colloid Subprogram Plan (DOE/ER-0384) or other Program documents can be obtained from Dr. Frank Wobber, Office of Energy Research (301-353-5549).

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ORGANIZATION OF THE MEETING

The meeting agenda (Appendix A) included two sessions of technical presentations. The first session discussed the difficulties in sampling and characterization of colloidal particles in groundwater and attempted to critically review innovative approaches. The second, and more extensive session critically reviewed observations of colloid movement in laboratory and field systems, with an emphasis on the chemical and hydrological factors controlling transport. In addition to platform presentations, a poster session was organized. The extended abstracts of contributions to both the platform and poster presentations make up the body of this meeting summary.

Although the oral presentations and discussion following those presentations addressed many of the important questions concerning colloid transport and deposition, two discussion sessions were organized to provide a forum to summarize the group concensus on important isues and try to resolve conflicting views. The first discussion session delt with natural conditions favoring colloid transport or deposition. The objective of the discussion was to identify natural environmental conditions of aqueous chemistry, mineralogy, hydrology, etc., that favor either the transport or the deposition of colloidal particles. The intent of this discussion is to focus research efforts on those natural subsurface environments with the greatest probability for occurrence of mobile colloids. The second discussion session was oriented toward the application of fundamental understanding of colloid mobililization and desposition to remediation or mitigation of contaminated aquifers. Several strategies to manipulate subsurface systems, particularly at waste sites, were discussed

The final session attempted to achieve a group consensus on research priorities for understanding the role of colloidal particles in the transport of contaminants in the subsurface environment. The draft of the DOE Colloid Subprogram Plan (2) was distributed to participants prior to the meeting and served as a focus for discussion.

This summary document will begin with a brief background review of the role of mobile colloidal particles on the subsurface transport of contaminants. This review is excerpted from McCarthy and Zachara (3).

BACKGROUND REVIEW OF THE PROBLEM OF COLLOID-FACILITATED TRANSPORT

Contaminants originating from the activities of man have entered the subsurface environment through waste disposal practices, spillage, and land application. Establishing effective disposal and isolation procedures for chemical wastes, protection of public health, and amelioration of subsurface contamination rely on the ability to predict the velocity at which contaminants move through the vadose and saturated zones. However, attempts to describe and predict contaminant transport cannot succeed if major pathways and mechanisms for transport are not accounted for.

Most approaches to describing and predicting the movement of contaminants treat groundwater as a two-phase system with contaminants partitioning between immobile solid constituents and the mobile aqueous phase. Many contaminants readily sorb to immobile aquifer media and are therefore generally considered to be virtually immobile in the subsurface, thus presenting little danger to groundwater supplies. For example, in soil and aquifer material many metals and radionuclides bind strongly to mineral components, while many nonpolar organic contaminants have a high affinity for binding to particulate organic matter. However, components of the solid phase in the colloidal size range may also be mobile in subsurface environments. Since the composition of colloidal particles is expected to be chemically similar to the surfaces of immobile aquifer material, these colloidal particles could also sorb organic and inorganic contaminants and stabilize them in the mobile phase.

Colloids are defined as particles with diameters less than 10 um (4). A variety of organic and inorganic materials exist as colloids in groundwater, including macromolecular components of "dissolved" organic carbon (DOC) such as humic substances, "biocolloids" such as microorganisms, microemulsions of nonaqueous phase liquids, mineral precipitates and weathering products, precipitates of transuranic elements such as plutonium, as well as rock and mineral fragments. The occurrence of colloidal particles in groundwater should not be surprising since colloidal-sized substances are known to be associated with the geologic matrices. For example, coarse-grained aquifer material can contain up to 5% clay-sized materials. A first but essential step in the genesis of mobile colloids in groundwater is the formation of a colloid suspension in the pore water, which can involve a number of mechanisms including (1) homogeneous nucleation of inorganic solids in the fluid phase, (2) release of colloidal material from the geologic matrix, and (3) translocation of inorganic and organic substances from the vadose or recharge zone.

Colloidal-size precipitates can form in the aqueous phase if geochemical gradients in groundwater pH, ion composition, redox potential, or CO_2 partial pressure induce supersaturation with respect to readily precipitable solid phases. Such gradients may result either from natural geochemical processes including microbiological activity that can reduce redox potential or influence CO_2 partial pressures or from contaminant infiltration. As examples, Gschwend and Reynolds (5) observed the precipitation of ferrous phosphate solids in groundwater beneath a sewage infiltration basin, and Fe-oxide colloids have been observed to precipitate in groundwaters as a result of both pH changes and oxygenation (6).

Colloidal materials can also be released to groundwater as a result of geochemical and biologic processes acting upon larger inorganic or organic particulate materials in the aquifer matrix. Organic macromolecules such as humic substances can be solubilized from kerogen, bitumen, or lignitic materials in the aquifer matrix as a result of microbial activity and abiotic hydrolysis. Bacteria attached to aquifer solids may secrete various exocellular materials or release cell fragments to groundwater.

Colloidal particles can also be released to groundwater if inorganic cementing agents that bind colloidal sized materials to larger mineral grains dissolve or if stable aggregates are deflocculated. Fe-oxide cements can dissolve under reducing conditions and release colloids in contaminant plumes containing levels of DOC high enough to promote microbial activity and anoxic conditions. The dissolution of iron oxides in oxide-cemented sand under anoxic conditions liberated layer silicate clays previously bound to the aquifer matrix (7). Similarly, siliceous colloidal material was released into groundwater in a calcareous environment because infiltration of waters of different composition dissolved the carbonate cements (8). Attached subsurface bacteria may become unattached under high nutrient/carbon conditions associated with contaminant plumes.

Colloidal particles in groundwater can also originate because of translocation from the vadose or root zone. Humic substances can be flushed from upper, organic-rich A and B soil horizons to the vadose and saturated zones during storm events and major periods of infiltration such as snowmelt (9). Although humic substances and microbes can adsorb to mineral surfaces, their movement to depth is apparently facilitated by transport through preferential flow paths through the porous media such as macropores and cracks associated with soil structure (10, 11). Layer silicate clays can also be mobilized from the soil zone by large storm events that lead to the infiltration of low ionic strength meteoric waters (12).

Stabilization of Colloidal Particles

The preceding discussion has shown how colloidal-sized material may be released from, transported to, or formed in groundwater. To be mobile over significant lateral distances and thus facilitate contaminant transport, suspended colloidal material must be stable (resisting aggregation with other like particles) and must not be susceptible to particle filtration in passage through porous media. Whether a particle will be stable, aggregated, filtered, or will settle in groundwater depends on its density, its size, the surface chemistry, the water chemistry, and the water flow rates in a complicated fashion that is not readily predictable from current understanding and models.

The stability of a homogeneous colloid suspension is determined by van der Waals attractive forces that promote aggregation and by electrostatic repulsive forces that drive particles apart. When electrostatic repulsions are dominant, the particles are electrostatically stabilized and remain in a dispersed state. Colloid stabilization is therefore influenced by particle mineralogy and surface chemistry and by other chemical factors controlling surface charge and the extent of the electrical double layer (13, 14). Even if hydrochemistry promotes their stability, suspended colloids can be mobile only if they are not filtered by the porous media. Particle filtration in groundwater can occur by physical straining or by physical/chemical collection by attractive surfaces on the immobile matrix. Straining filtration is controlled by the pore dimensions and geometry relative to the colloid particle size, but may be of secondary importance for most groundwater colloids because their size is sufficiently small (typically 1 um or less) to permit them to move unimpeded through the large pore spaces of sandy aquifers (15). Filtration by physical/chemical collection is controlled by phenomena similar to those described for particle-particle interactions, except the colloidal particles associate not with other particles, but with the mineral or organic components of the immobile aquifer media. Collection of colloids is favored on surfaces of opposite charge. Negatively charged colloids, including humic substances, are expected to be more mobile than positively charged particles because most groundwater matrices carry net negative charge. Adsorption of humic substances can impart a negative surface charge to colloids such as oxides, layer silicates, and calcium carbonate with positively charged surface sites and thereby increase the stability and mobility of these particles. Ryan (7) postulated that coatings of adsorbed humic substances developed a negative charge on mobile layer silicate and Fe-oxide colloids in anoxic Atlantic coastal plain groundwaters.

Stable colloids in groundwater can be mobile even under conditions that favor physical/chemical collection if particle surface collisions are minimized by slow interpore transport rates or if water movement occurs through preferential flow paths with high relative velocity. Thus, Harvey et al. (16) found that larger microspheres were transported greater distances than smaller ones in a permeable sand aquifer and suggested that the larger spheres experienced fewer diffusion-induced particle-surface collisions that could lead to attachment or collection (20). Microorganisms and organic macromolecules have been transported through aquifers and intact soil cores more rapidly than chemical tracers because their movement is limited to channels and to the secondary pore structure rather than extending through the intergranular pore space (16-18).

Implications of Colloids for Contaminant Transport

If organic and inorganic colloidal particles are present and mobile in groundwater, can they facilitate the transport of contaminants? Knowledge of the chemical mechanisms of contaminant-colloid interactions and our capabilities to predict the extent of the association varies widely depending on the nature of the contaminant and the type of colloid. Furthermore, much of the information is drawn from studies of colloidal material in surface waters, while very few data are available for colloids isolated from groundwater.

Humic substances from soil or surface water are known to bind hydrophobic organic contaminants, enhance the pollutant's apparent solubility in water, and reduce its apparent affinity for binding to sediment particles and to immobile phase of reverse-phase chromatographic columns and soil columns (19-21). Furthermore, the polyelectrolyte character of humic and fulvic acids enables them to associate with metal ions. Laboratory and field studies have demonstrated the significance of humics on the speciation of metals (22) and radionuclides (23). Humic and fulvic acids from soil and sediment bind actinides strongly (e.g.,24), and colloidal organic matter from lakes also bind radionuclides and inhibit their adsorption to sediments (23). Inorganic colloidal particles in groundwater also strongly adsorb contaminants. Layer silicate clays adsorb metallic and organic cations by ion exchange (25). Surfaces of Fe-, Mn-, Al-, and Si-oxide particles strongly adsorb certain metallic cations and organic and inorganic acid anions (26). Metals and organic acids may adsorb to the surface of calcium carbonate by complexation or exchange with structural ions (27).

The association of contaminants with colloidal material has been demonstrated in groundwater. Both transition elements and lanthanide radionuclides were associated with inorganic colloidal particles in groundwater outside a nuclear detonation cavity at the Nevada Test Site (28). In groundwater downgradient from a uranium ore deposit in Australia, uranium and daughter species such as thorium were sorbed to Fe- and Si-rich colloidal particles between 0.018 and 1.0 um in size (29). Radioactive cobalt and uranium were associated with high molecular weight organic material in groundwater near a disposal trench at the Oak Ridge National Laboratory (30). Likewise, radionuclides in groundwater of four contaminant plumes at the Chalk River Nuclear Laboratory in Canada were associated with anionic organic ligands in the 500 to 10,000 molecular weight range (31). Furthermore, insoluble metals and radionuclides may themselves form colloidal-sized precipitates which may be mobile (5, 32).

Implications of Colloid Mobility on Hazardous Waste Management

Manipulation of colloid mobilization and deposition could be a useful tool for mitigation or remediation at waste sites. For example, if aquifer remediation is a goal, then removal of highly adsorbed contaminants from groundwater could be enhanced by controlled mobilization, collection, and treatment of colloidal particles from the impacted ground water zone. Colloid mobilization may affect aquifer permeability, however, and the benefits of contaminant solubilization vs pore clogging must be carefully assessed. In many cases, removal of existing contaminants is not necessary or desirable. Effective waste management may require only that the migration of colloid-associated contaminants be contained within the boundaries of a controlled waste facility. It may be sufficient simply to limit the magnitude of this vector by treatments that promote deposition of colloids.

Therefore, improved understanding of the mobilization and deposition of colloidal particles in groundwater has application not only in solving problems of colloid-facilitated contaminant transport, but also in developing generally applicable strategies for in situ isolation or remediation of hazardous wastes.

Research Needs

The weakness of current predictive capabilities highlights the inadequacy of our understanding of mechanisms controlling the transport of highly retarded contaminants. Accurate assessment of current contaminant problems, engineering of containment strategies, and cost-effective remediation approaches can all be improved by a fundamental understanding of transport processes. While existing data suggest that mobile colloidal particles may be an important mechanism of contaminant transport through the vadose zone and within the saturated zone, this information is largely anecdotal and is inadequate either to evaluate the general significance of the phenomena or to develop a capability to include colloid-facilitated transport in computer models that predict contaminant migration in the subsurface (3). To fully describe and account for colloid-facilitated transport of contaminants in groundwater, and to develop strategies to utilize colloid mobility for waste management or aquifer remediation, DOE has identified a subprogram of the Subsurface Science Program to address several major questions concerning subsurface colloids (2), including the following:

1. Are colloids present in groundwater, and how do we sample them without introducing artifacts? Why are colloids present in groundwater; can the presence of stable colloids be understood and predicted based on the mineralogy and hydrochemistry of specific subsurface environments? What is the composition, physicochemical nature, and abundance of colloidal particles in subsurface environments?
2. Do colloids move through aquifers? Can the chemical and hydrologic factors controlling the stabilization, transport, and deposition of colloidal particles be described and incorporated within predictive transport models?
3. Do mobile colloids sorb and transport contaminants? What is the capacity of groundwater colloids to bind contaminants? To what extent and by what mechanisms do chemical and radioactive contaminants either precipitate as colloidal-sized particles or sorb to other colloidal material?
4. Can improved understanding of the biogeochemistry of subsurface colloids be applied to devise mitigation and remediation strategies based on manipulation of colloid mobilization or deposition?

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SESSION I.

SAMPLING AND CHARACTERIZATION OF COLLOIDAL PARTICLES IN GROUNDWATER

Moderated by Philip M. Gschwend [Massachusetts Institute of Technology]

Objective of the Session: To discuss difficulties in sampling and characterizing colloidal particles in groundwater and critically review innovative approaches.

Titles and Authors of Platform Presentations:

Introduction to Sampling Problems
P. Gschwend [Massachusetts Institute of Technology]

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INTRODUCTION TO SAMPLING PROBLEMS

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As a prerequisite to all studies of colloids in groundwater and the roles they may play, we must assure ourselves that procedures used to obtain groundwater colloids recover suspensions as they occurred belowground. Most sampling methods currently employed to investigate groundwater probably cause the inclusion of submicron particles which were not suspended in the subsurface either due to physical (e.g., shearing of immobile soil colloids) or chemical (e.g., precipitation of iron oxides) artifacts. To avoid these problems, we have utilized a sampling procedure which features prolonged (hours) slow (~100 mL/min) pumping and handling the samples so as to minimize any atmospheric contact (0_2 or CO_2 exchange). Tests of this extended pumping at sites in New Jersey, Delaware, and New York always show initially high turbidity, which declines to much lower concentrations of colloids over several hours. At background wells, the light scattering intensity, which measures colloid presence, becomes indistinguishable from distilled water controls; on the other hand, at wells screened in subsurface waters which have undergone some chemical change, the light scattering levels off at intensities well above background suggesting substantial colloidal presence (1 - 100 mg/L). Several lines of evidence support the contention that these colloidal suspensions were actually suspended in situ: (1) the observed microparticles are small enough not to settle rapidly (SEM observations), (2) they exhibit surface charge characteristics which would inhibit heterocoagulation with the aquifer solids (microelectrophoresis observations), and (3) they appear to be geochemically stable relative to the local groundwater chemical composition (SEM-EDAX observations of particles collected on 0.03 μm Nuclepore filters). Since wells installed in the same geological strata by the same techniques at the same time and sampled in the same way do not reveal similar colloidal levels, we believe our sampling approach has been successful in acquiring groundwater colloids actually moving through the subsurface.

CHARACTERISATION OF GROUNDWATER COLLOIDS APPROACHES AND LIMITATIONS

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The potential role of colloids in the migration of contaminants in aqueous media was outlined with particular reference to the transport and retention of radionuclides from nuclear waste (1). The formation and potential sources of colloids which may arise was considered. This included a description of nucleation and growth mechanisms, as illustrated with reference to processes involving cation hydrolysis and polynuclear ion formation. The role of groundwater colloids such as clays and organic polymeric substances (humic acids) was discussed, as was the importance of colloid interaction forces (Coulombic, Dispersion, Steric Stabilization, Hydrophobic effect) in the stability and migration of colloids. The nature of these interactions in aqueous systems were described with particular reference to the mechanisms of surface charge development with lyophobic colloids. With larger colloid particles (> 0.1 um) the effect of a shallow secondary minima (< 10kT) in the interaction potential may be highly significant for our understanding of the in situ behavior of colloids in groundwaters. Such an effect may give rise to weak colloidal aggregates and transient deposition behavior on mineral surfaces. The importance of surface charge and interfacial structure on colloid sorption and characteristics was also illustrated.

An outline of a range of techniques which may be valuable in colloid characterisation was given. These include ultrafiltration, centrifugation, and various light scattering techniques (static light scattering, photon correlation spectroscopy, electrophoretic light scattering, fibre optic light scattering). The information obtainable and limitations of these techniques was discussed for both model systems (oxides, clays) and environmental colloids.

The latter include investigations of colloids firstly in groundwaters and leachates derived from cementitious systems and secondly in marine and estuarine waters. Colloid behavior in such systems is complicated due to the complex water chemistry (pH, E_h, ionic strength) and a better understanding may be obtained by applying a combination of sampling, separation and characterisation techniques.

Because concrete may be used as an immobilizing medium and repository construction material for radioactive waste disposal the mechanisms of formation and characteristics of colloids generated in such an aqueous environment are of importance. Recent investigations have shown that oligomeric species and colloids containing predominantly silicon and aluminum are generated in aqueous cementitious media (2). These have been characterised extensively using a range of techniques including light scattering, PCS, electrophoresis, scanning electron microscopy (SEM), and EDAX. Inductively Coupled Plasma Emission and Mass Spectrometry (ICP-OES & ICP-MS) have been applied in the study of the nucleation and growth of calcium silicate and aluminate colloidal species in solution also to establish the mechanism of radionuclide (Cs, Co, Ni, Eu, Ce, U, Th) incorporation and sorption mechanisms which may arise with such systems. The marked effect of ionic strength (Ca^{2+}) on the stability of sorption behavior of natural colloids in such a cementitious environment is also another aspect of importance here.

Another complex system where the mechanism of sorption is related to the physico-chemical characteristics of colloids in an aqueous medium arises in marine and estuarine waters. The distribution of traxce radionuclides at environmental levels, in particular actinides (Pu, Am), in heterogeneous sediments and marine colloids is dominated by such effects. A combination of separation and characterisation techniques coupled with sensitive α-spectrometry can give an insight into the mechanism of uptake and the nature of sorbed species (3).

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NATURAL COLLOIDS AND GENERATION OF ACTINIDE PSEUDOCOLLOIDS IN GROUNDWATER

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Natural colloids are ubiquitous in groundwaters and by introducing actinide ions they readily generate actinide pseudocolloids through sorption [1,2] or ion exchange process [3,4]. The chemical composition and size distribution of natural colloids are different from one groundwater to another depending on the geochemical properties of each given aquifer system [5]. They are composed of inorganic oxide or hydroxide aggregates if the groundwater is poor in organic substances, or of organometallic polymer coagulates if the aquifer system contains humic substances which are the most common organics in groundwater [3]. All natural colloids contain a large number of trace heavy metals, rare earth elements (REE), Fe, Zr, Hf, Th, U, etc. [4], which are chemically natural analogues of actinides and some fission products. Such tracer elements concentrated heavily on colloids in groundwater are direct evidence for that actinide ions may easily undergo the generation of pseudocolloids in a given groundwater. Most of groundwater colloids play a role of scavenging carrier for aquatic actinide ions which are present as high oxidation sate ($Z \geq 3+$) and thus hydrolysed always in neutral aqueous solution.

Characterization

In deep groundwater, the age-old geological contact of water with surrounding geomatrices yield solubility equilibria of a wide variety of elements and also generates colloids which contain many heavy metal elements as trace constituents. A typical example of the inorganic composition of colloids in one of Gorleben groundwaters is illustrated in Table 1 [1], along with different sizes of colloids collected on ultrafilters of decreasing pore size. The concentrations of element analyzed in colloids collected by parallel ultrafiltrations at various pore sizes are normalized to one liter groundwater.

Table 1Analysis of trace elements in the Gohy^{-1012} groundwater and colloids (concentration in mol/L[a] [1]

Element	Groundwater	Groundwater-colloids[b]			
	(0.45μm)	XM 300	XM100 A	XM 50	YM 5
		(15 nm)	(5 nm)	(3 nm)	(-1 nm)
Ba	7.0x10^{-9}	ND[c]	2.7x10^{-8}	ND	3.7x10^{-8}
Br	1.9x10^{-6}	7.7x10^{-9}	1.1x10^{-8}	1.1x10^{-8}	1.2x10^{-8}
Ca	2.6x10^{-4}	2.5x10^{-5}	3.7x10^{-5}	5.7x10^{-5}	7.9x10^{-5}
Ce	3.2x10^{-8}	0.7x10^{-8}	1.2x10^{-8}	1.3x10^{-8}	1.6x10^{-8}
Co	2.2x10^{-8}	ND[c]	3.4x10^{-9}	1.3x10^{-9}	2.2x10^{-9}
Cr	4.2x10^{-8}	1.0x10^{-8}	1.4x10^{-8}	1.5x10^{-8}	1.6x10^{-8}
Eu	1.8x10^{-9}	6.7x10^{-10}	9.4x10^{-10}	8.2x10^{-10}	1.1x10^{-9}
Fe	3.7x10^{-6}	3.1x10^{-6}	3.4x10^{-6}	3.5x10^{-6}	3.6x10^{-6}
Hf	3.8x10^{-10}	0.7x10^{-10}	1.2x10^{-10}	1.2x10^{-10}	1.5x10^{-10}
La	1.6x10^{-8}	3.1x10^{-9}	4.8x10^{-9}	5.2x10^{-9}	6.2x10^{-9}
Nd	2.3x10^{-8}	5.1x10^{-9}	ND[c]	5.4x10^{-9}	6.3x10^{-9}
Sb	1.6x10^{-9}	1.3x10^{-10}	2.3x10^{-10}	3.1x10^{-10}	1.2x10^{-9}
Sm	4.2x10^{-9}	6.3x10^{-10}	1.0x10^{-9}	1.1x10^{-9}	ND[c]
Th	3.2x10^{-9}	1.5x10^{-9}	2.2x10^{-9}	2.6x10^{-9}	2.7x10^{-9}
U	5.5x10^{-9}	6.3x10^{-10}	5.3x10^{-10}	5.4x10^{-10}	2.1x10^{-9}

[a] Groundwater is filtered by a Millipore filter of 0.45μm and groundwater-colloids are collected by different Amicon filters as indicated. The concentration of each element in colloids corresponds to its amount in 1 lite groundwater.

[b] Amicon filter description (estimated pore size in parentheses) above columns.

[c] Not determined.

In the Gorleben aquifer system, groundwater colloids are found mostly as humic colloids [3,4]. The average size of these aggregates is considerably larger than the average molecular size of humic acid (ca, 11000 Dalton) separated from the same groundwater [6]. The ultrafiltration has confirmed that the major part of trace heavy metal ions, i.e., chemical analogues of actinide ions, in groundwater is quantitatively associated with humic colloids and therefore the concentrations of these ions increase with increasing the humic colloid concentration [4].

Generation of actinide pseudocolloids

The actinide ions introduced in Gorleben groundwaters are sorbed on humic colloids present, thus producing their pseudocolloids, which can be then filtered almost quantitatively by ultrafiltration at the smallest pore size (ca. 1 nm) [2,7]. The generation of pseudocolloids is corroborated as an ion exchange process; the reversibility is attained by changing pH of the solution [4]. In a groundwater poor in humic substances, colloids are of inorganic nature, composed o metal ions of trivalent and higher oxidation state, which are sensitive to hydrolysis. Such inorganic colloids are much less stable than humic colloids, do not sorb trace actinide ions quantitatively and thus the generation of actinide pseudocolloids is less prevalent.

Speciation by laser induced photoacoustic spectroscopy (LPAS)

The application of laser-induced photoacoustic spectroscopy (LPAS) [8,10] has been made for the identification and number counting of groundwater colloids [5,9]. The method, named as photoacoustic detection of laser light scattering (PALD), is based on the time resolution of photoacoustic signals generated from absorption and scattering of the incident light. The time resolved two photoacoustic signals, processed by a Boxcar, provide a possibility of identifying the nature of colloids, i.e., inorganic or organic origin, as well as of counting colloid population. Using Dow-latex particles of different sizes as calibration standards, photoacoustic signals generated by scattered light and monitored directly on a piezoelectric transducer are correlated to the colloid size and concentration. Colloids can be counted down to 10^8 particles/L for the size as small as 1 nm. Photoacoustic signals produced by absorption of light gives information on the colloid composition. A number of Gorleben groundwaters rich and poor in colloid are characterized for their population and nature of colloid.

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SAMPLING AND CHARACTERIZATION OF COLLOIDS IN THE CANADIAN NUCLEAR FUEL MANAGEMENT PROGRAM

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Atomic Energy of Canada Ltd. (AECL) has been studying the geochemistry and hydrology of groundwater as part of a program to evaluate the concept of used fuel disposal at depth in plutonic rock. The objective of the colloid program at AECL has been to evaluate the role of colloids in radionuclide transport through the geosphere. Assuming colloids formed in the disposal vault will not escape through the buffer material, emphasis has been placed on radiocolloid formation by radionuclide sorption on natural colloids. To assess the likelihood and importance of radiocolloid formation in deep groundwaters (to a depth of 1000 m) data is needed on the concentration, size distribution, and composition of natural groundwater colloids. In addition, the sorption properties of radionuclides on natural colloids must be evaluated. After the importance of radiocolloid formation has been established our attention will have to focus on colloid migration through fractured media.

Colloid sampling programs have been carried out mainly at the Cigar Lake uranium deposit in Northern Saskatchewan (1)(2), and in the Whiteshell Research Area (WRA) in Southern Manitoba. The Cigar Lake deposit is a sandstone hosted uranium ore body at a depth of 400 m, which is being studied as a natural analog to a used fuel disposal vault. The WRA is a fractured granite environment representative of the host rock considered for a disposal vault in the Canadian waste management concept. Colloid sampling has also been carried out at the Grimsel Test Site as part of an interlaboratory comparison exercise.

At Cigar Lake and WRA, groundwaters from depths of 100 to 900 m have been sampled from HQ boreholes with 7.6 cm diameters. The boreholes were lined with either West Bay casing or another form of PVC tubing, although a few holes contained AQ drill rod made of black carbon steel. The sample zones were isolated with rubber or neoprene packers. Groundwater was recovered from the boreholes with air or nitrogen operated squeeze pumps, which can recover water at a rate of 70 to 500 mL/min. In order to avoid atmospheric contamination the groundwater was collected in 50 L nitrogen-flushed carboys or else it was pumped directly into a nitrogen flushed glove box for filtration.

Since the concentration of particles in natural groundwaters is low, colloids were concentrated from 50 L samples using Millipore tangential flow ultrafiltrations systems, protected from atmospheric contamination by a glove box. Initially particles greater than 10,000 molecular weight (MW) were separated into a 2 to 3 L concentrate using the Pellicon ultrafiltration system, equipped with a filter cassette having an active surface area of 4600 cm^2. The concentrate was further divided into a fraction containing colloids between 1 and 450 nm and a fraction enriched in particles greater than 450 nm, using the Minitan ultrafiltration system equipped with a Durapore membrane with an active surface area of 240 cm^2. The groundwater was not prefiltered before particle concentration to avoid colloid losses to the prefilter.

Although this filtration scheme has worked rather well, the method of colloid separation was modified recently to minimize potential problems of salt retention in the colloid concentrate and particle entrapment in the Pellicon cassette. Although salt retention is not supposed to occur with 10,000 MW membranes, experience has indicated that the salt concentration may increase in the colloid concentrate (1 percent) if high transmembrane pressures are used during ultrafiltration. To minimize the risk of salt retention the initial particle concentration is now done with a 100,000 MW membrane. For this initial filtration the cassette was also replaced with filter packets separated with retentate screens or linear channels. This new arrangement allows one to pass larger particles through the filter system and to separate filter packets for cleaning. The filtrate passing the 100,000 MW filter is collected and filtered with a 10,000 MW cassette.

The concentration and size distribution of particles was measured by pressure filtering particle concentrates through a series of Nuclepore filters. The concentrate with particles greater than 450 nm was filtered in series through 10000, 5000 and 400 nm membranes, while the colloid concentrate was passed through 100, 50 and 10 nm membranes. Since particle concentration is determined by the weight of material deposited on a Nuclepore membranes, samples with a high salt content required a rinse with about 10 ML of deionized water after filtration. Qualitative compositions of particles larger than about 1000 nm, which were deposited on Nuclepore membranes, were obtained with SEM/EDS. XRD analysis of particles separated onto silver membranes was used to identify the dominant mineralogy of groundwater particles. More information on colloid composition and natural radiocolloid formation was obtained from a chemical and radiochemical analysis of filtered water and the various particle concentrates.

When particle concentrations are expressed as mg/L the total particle concentration is often dominated by particles larger than 450 nm. In about 35 percent of the samples from Cigar Lake and WRA particles greater than 450 nm make up more than 90 percent of the total particle concentration. In the other samples colloids (10 to 450 nm) make up from 10 to 90 percent of the total particle concentration. Particle (>450 nm) concentrations were between 0.03 and 22 mg/L. Compared to WRA, the concentrations of particles and colloids at Cigar Lake were generally higher.

From SEM/EDS, XRD and chemical analysis of particle concentrates it is apparent that groundwater particles may consist of clay minerals, common rock forming minerals (quartz, feldspar), Fe and Si oxides, carbonate, and organics (bacteria, humic acid, unidentified material). The association of naturally occurring radionuclides (U, Th and Ra-226) with colloids depends upon the particle concentrations in groundwater. Table 1 summarizes the percentage of each radionuclide in groundwater which is found associated with particles.

Table 1

PERCENTAGE OF RADIONUCLIDES ASSOCIATED WITH PARTICLES

	Cigar Lake	WRA	Grimsel
U	6 to 90	0.3 to 70	10
Th	0 to 100	0 to 70	
Ra-226	0 to 70	0.3 to 20	10

The size distribution of uranium associated with particles was determined by filtering particle concentrates through Nuclepore filters with different sizes. In general, the uranium size distribution reflected the size distribution of particles recovered from groundwater.

During the sampling and concentration of colloids from deep groundwaters one of the greatest challenges is the prevention of atmospheric contamination, which may oxidize dissolved Fe(II) or upset carbonate equilibrium. Although the use of nitrogen flushed collection vessels and portable glove boxes minimize the risk of atmospheric contamination, the effectiveness of these barriers must still be assessed. The development of a downhole filtration system may allow us to evaluate changes in colloid samples caused by atmospheric contamination or by sample depressurization. Another consideration is the effect of groundwater pumping on particles sampled from groundwater. Except for artesian wells, groundwater cannot be sampled without pumping. One must also evaluate the effects of borehole contamination introduced by drilling fluids (oil, bacteria, mud, diatoms) or in some cases corroding steel pipes. Since colloids may coagulate after being concentrated, size analysis should be carried out shortly after particle concentration.

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SAMPLING AND ANALYSIS OF COLLOIDS IN GROUNDWATER AT THE NEVADA TEST SITE

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The occurrence and properties of colloidal material in groundwater is of general interest to the understanding of contaminant transport. Colloidal particulates may play an important role in increasing the rate of transport of both organic and inorganic pollutants in the subsurface environment (1,2). At the Nevada Test Site (NTS) it appears that association with colloidal material may have increased the transport of radionuclides away from a nuclear detonation cavity (3). Most models of contaminant transport do not take partitioning of the contaminant to colloidal particles into account. The work presented here was directed at obtaining some fundamental information pertinent to colloidal transport at the NTS. This constituted a preliminary study to provide information in four areas:

1. What is the occurrence of colloidal material on and off the NTS? Are mass per liter burdens of colloids different in different hydrologic regimes with different water chemistries?
2. What is the chemical composition of the colloidal material?
3. Are there variations in the composition of colloidal particles at NTS in waters with different chemistries?
4. Can estimates of K_D values be made on the small amounts of colloidal matter extracted from NTS groundwater samples? How do these values compare to those determined from bulk material?

Occurrence of colloidal particulates at NTS -- In August of 1987, spring and well samples were collected from ten sites on the NTS and thirteen other sites in southern and central Nevada. The sites were selected to provide samples of water with carbonate, volcanic or alluvium source rock. Five gallons of water were collected at each site; no attempt was made at preserving the sample.

The mass loadings of colloidal particles was determined by serial ultrafiltration using 1.0, 0.4, 0.1, and 0.03 μm membrane filters. The filtration was performed using stirred filter cells pressurized with air. Well samples have higher concentrations and are slightly more dispersed about the mean than spring sites, except in the 1.0 to 0.4 μm range where similar populations are represented. The higher concentrations reported for wells may be caused by artifacts introduced during sampling. For example, pumping subjects the formation to abnormally high gradients which may detach particles from the formation. Formation disturbances caused by well construction and development may also result in collection of samples with high apparent colloid concentrations. Springs flow under natural gradients and have none of the disturbances associated with wells. Therefore, the reported spring concentrations may be more representative of actual background levels. NTS and off-NTS sites contain similar colloid populations. This suggests that detonation shock waves on the NTS do not substantially increase particle release from the formation. However, the mass loadings observed are considerably lower than those reported for cavity samples (3). Volcanic and carbonate sites represent similar populations in the colloidal range with mean concentrations in each size cut of less than 0.3 mg/l. There is insufficient data to discuss the alluvial water samples.

An alternative to ultrafiltration was necessary for very fine particles due to the unavailability of suitable filters below 0.03 μm. The next available filter is 0.003 μm but has a paper backing that makes mass determination impossible. Size exclusion chromatography (SEC) was used to estimate relative particle size distributions below 0.1 μm. Size calibration is usually done indirectly using globular proteins and synthetic polymers of known size and shape; however, interpretation of SEC data may be complicated by adsorption and ion exclusion effects. Solids from well U20N were collected by Buddemeier's group at Lawrence Livermore National Laboratory (LLNL) by ultrafiltration. The dry sample which was mixed with distilled water and sent to a commercial lab for SEC analysis. Three peaks were observed and were attributed to particles larger than 50 nm, particles about 40 nm, and particles smaller than 25-35 nm (the column used had a pore size of 100 nm).

Composition of colloidal particles from springs and wells at NTS -- Due to the small size of the particles X-ray diffraction spectrometry (XRD) was impractical. Such small sized particles would have very broad diffraction peaks if any at all. Therefore compositional analysis was performed using infrared spectrometry. Infrared spectrometry provides good qualitative and quantitative data complimentary to XRD. Unlike XRD it is useful for both crystalline and amorphous material and is suitable for both inorganic and organic material analysis. The measurements were made on a research grade Fourier transform infrared spectrometer (FTIR). The FTIR provides for very accurate wavelength determination ($0.003cm^{-1}$) referenced to a helium-neon laser. Samples were prepared by mixing the ultrafiltration retentates with potassium bromide and pressing into disks using an hydraulic press.

All the spectra show the presence of organic material as evidenced by absorbance at the frequencies associated with C-H stretching; the shape of the infrared absorbance band in this region indicates aliphatic CH2 and CH3. Some samples have infrared absorbance in the 1730 cm-1 region indicating the presence of carboxylic acid functionality. These same samples also possess absorbance bands in regions associated with the amide group. These samples can be interpreted as being mineral by bulk composition but containing an organic coating, possibly humic material.

Those samples showing only C-H strength with no organic oxygenate or amide infrared absorbances most likely have some contamination by oil. This oil would most likely be a simple paraffinic lube oil. The possibility of sample contamination in handling can not be ruled out.

In addition to the organic matter, infrared absorbance from SiO2 is clearly evident. Fused silica in indicated (1162, 1099, 802, and 460 cm-^{1}, another crystalline form such as cristobalite may also be present (1100, 800, 480cm-^{1}, 430) and amorphous silica is indicated (1109, 802, 470 cm-^{1}). The peak near 1100cm-^{1} is attributed to the bridging oxygen in a Si-O-Si polymer. The Si-O-Si stretching frequency shifts to higher values (e.g. 1162 cm-^{1} with increased corner-sharing of SiO4 tetrahedra. The weak bands below 1000 cm^{-1} are useful in identifying specific silicates such as montmorillonite or albite. To date we have not been able to identify a specific mineral other than amorphous silica, fused silica and possibly cristobalite. Some samples show infrared absorbance at 475 and 515 cm-^{1} which may be indicative of alkali fedspars.

Adsorption properties of colloids sampled at NTS -- In conjunction with Bob Buddemeir and Joann Rego at LLNL we attempted to determine the Kd values for cesium-137, cobalt-60, atimony-125, and europium-152. These measurements utilized radioactive isotopes prepared by LLNL and "pre-concentrated" colloidal suspensions prepared by our group. The concentration enhancement was accomplished by partial ultrafiltration of water samples from water well 20 (3.9 liters were reduced to 280 ml). A 0.40 um filter was used so that the material above the filter became enriched in colloidal mass. The goal was to enhance the mass per liter values of colloidal particulates with minimal perturbation of the dissolved salt concentrations. Chemical analysis of the dissolved salts in the enriched solutions matched those of the starting solutions quite well, assuring no change in ionic strength or major ion concentrations. A sample of the final concentrate was desalted using a 0.003 micron polycarbonate filter and repeated washing with deionized water during the ultrafiltration. This was reduced in volume to about 15 ml which was then dried over a steam bath and weighed. This gave the colloidal concentration to be 36 mg/l in the concentrate.

The concentrated colloid suspensions were spiked with measured aliquots of the individual isotopes (in separate experiments) of pre-determined activity. The spiked solutions were then allowed to equilibrate for a week. The spiked colloids were injected into the SEC and fractions collected as material eluted. Our goal was to determine the activity in the eluting colloids relative to the eluting salt peak. However little or no radioactivity was detected in the eluted samples! All the radioactive material eluted well after the salt peaks indicative of strong adsorption to the column material [In preparation for this study non-radioactive cesium salts were chromatographed on the SEC to be certain that they did not strongly sorb to the column material. In these experiments there was no indication of cesium absorption at all. We have no explanation of this contradiction.]

Because of the difficulties in using SEC the radionuclide adsorption experiments were performed using μm ultrafiltration membranes. The spiked samples were filtered through a 0.03 μm filter in a stir-cell and the retentates given a 5 ml rinse in distilled water. The filter was counted and the filtrate was passed through a 0.003 μm filter which was also given a 5 ml rinse and counted. The filtrate at this point should have no filterable mass larger than 0.003 μm. As a check on adsorption of radionuclide to the filter the filtrate from the last step was again subjected to the same filtering procedure just described.

The KD calculations were made assuming that (1) the radionuclide concentration is sufficiently high that it is unaffected by adsorption to either the filter or the colloids (i.e. only a small fraction of the total available is adsorbed) and (2) the adsorption is linear and reversible. A simple treatment of the data showed apparently no adsorption on the colloid for antimony or cesium. In the case of europium there was strong adsorption, in reasonable agreement with values reported for tuffaceous material. K_D values could not be determined for the 0.003 μm retentates.

Conclusions -- The conclusions drawn from this study are:

The occurrence of colloidal material in groundwater at the NTS is ubiquitous but with no clear trend for mass loadings with variation in the water chemistry.

The colloidal material composition varies considerably. In one instance it was predominantly calcium carbonate, which may have precipitated out as a result of CO_2 degassing.. In most cases the material is colloidal silica with varying ratios of silica polymorphs. This variation occurs from site to site as well as between particle size ranges.

Variation of particle composition with water chemistry is expected but not clearly observed. The detection of a pure carbonate colloid and an almost pure silica colloid support the notion that the local water chemistry may profoundly effect the particle composition. This is less evident in cases where there is greater inhomogeneity in the colloid composition. This may be an important consideration when dealing with transport of colloidal material into different chemical regimes. The source of the organic fraction associated with some samples is unresolved.

Colloidal material removed from Nevada spring and well water is shown to selectively absorb radionuclides.

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AN APPROACH TO STUDYING RADIONUCLIDE TRANSPORT BY COLLOIDS IN NATURAL ROCK/WATER SYSTEMS

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The migration of radionuclides within the geosphere at a radioactive waste repository is largely governed by movement of the groundwater. The transport models used in safety assessment studies typically include the processes of advection, diffusion and retardation by rock/water interactions. Since natural groundwaters contain colloidal particles in the size range 1 nm-1μm which may have radionuclides associated with them, there is another pathway by which radionuclides released at a breach of the near field barrier can travel through the geosphere. In the case of normally insoluble elements such as thorium, radionuclide-colloid association could have a marked effect on thorium migration. Even for soluble elements the presence of colloids could provide alternative pathways which may make untenable the use of linear distribution factors for the partition of radionuclide activity between solid and liquid phases.

Work on understanding the nature and properties of natural colloids and their association with radionuclides has only been carried out relatively recently. The subject is complex due to the variety of colloid types based, for example, on iron oxides, clay minerals, detrital silica, calcite and organic macromolecules such as humic substances. Radionuclides may form colloids directly (real colloids), or be associated with naturally occurring colloids (pseudocolloids). In addition, their small size and relatively large surface area and consequent reactivity, which can result, for example, in aggregation or dissolution under changing chemical conditions or exposure to atmosphere, means that great care must be taken in sampling them from aquifers, and in their subsequent characterisation in the laboratory.

In order to find out whether the presence of radionuclide colloid association will lead to changes in radionuclide mobility with the consequent need for such effects to be included in transport models, a programme of study has been undertaken at Harwell beginning with a characterisation of colloids from several different aquifers and leading to studies of colloid mobility using labelled colloids in both laboratory and field experiments, and of colloid generation due to near field barrier breakdown.

As in other experiments concerned with radioactive waste disposal it is important to combine laboratory experiments over a small timescale and short distances, with field experiments over larger distances, and the use of natural analogue sites where the result of previous radionuclide transport over geological timescales may be assessed.

One of the main techniques used here is the determination of the activities of the longer-lived actinides in the natural decay series using isotope dilution/alpha and mass spectrometry. The former technique is capable of measuring isotopic activities in mineral phases and in groundwater for example down to ~10 ppt uranium or thorium. In addition, determinations of daughter parent activity ratios within the decay series, and their divergence from a value of unity expected for secular equilibrium, will give an idea of the previous geochemistry of the system studied and with additional supporting information lead to the association of timescales to past geochemical events. Thus the geochemical stability of a given system may be assessed.

The low actinide activities in natural groundwaters result in the need for relatively large water samples 10^2-10^3 liters for accurate measurements using alpha spectrometry. In order to measure the activities associated with colloids it is convenient to concentrate the colloid population on sampling within the solution phase and in isolation from the atmosphere using an ultrafiltration technique.

Such a sampling technique (1) based on tangential flow ultrafiltration has been used in the study of several aquifers (2, 3, 4,). The partition of uranium and thorium isotopes between the phases present in the groundwater, particulate (>1 μm), colloid and solution phases has been measured, and the range of values obtained for the activity fraction associated with the colloid phase has been determined.

Inductively Compled Plasma Optical Emission Spectroscopy (ICP/OES) has been used to determine the major and minor ions present, particularly in the colloidal phase. Physical characterisation has been carried out using Scanning Electron Microscopy (SEM), Photon Correlation Spectroscopy (PCS) and microelectrophoresis. The range of colloid particle sizes has been measured using SEM and PCS, while the former technique gives the colloid concentration and some idea of their elemental composition.

The stability of natural colloids depends in part on their electrical charge or potential, conveniently determined from mobility measurements using microelectrophoresis. Again, the size and magnitude of the mobility can indicate colloid composition.

The results of these measurements at aquifers based on weathered schists, sandstone and fractured granite and slate were discussed. The fraction of total actinide activities associated with the colloid phase is found to be of the order of a few percent for thorium and less than one percent for radium. Colloid populations in the range 10^8-10^{10} particles/litre were determined from SEM analysis with its inherent lower size limit of about 30-50 nm. The measured mobilities in all cases were negative and the combination of SEM and mobility measured is used to indicate the likely colloid compositions.

The next stage of these investigations involving measurements of colloid migration is now in progress.

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DISTRIBUTION AND CHARACTERIZATION OF BACTERIA IN DEEP AQUIFERS

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Microbiologists virtually ignored subsurface environments (i.e., everything beneath the true topsoil zone, or A horizon, of the earth's crust) for many years (ca. 1915-1980) because it was generally believed that such environments were almost devoid of microbial life. In the early 1980's however, several developments led to a renewed interest in the subsurface on the part of microbial ecologists. Among these developments were (i) a recognition of sporadic, unconfirmed reports describing the occurrence of microbes at depth, (ii) the development of new methods for the detection of microbes in environmental samples, (iii) rapidly increasing concern about subsurface (especially groundwater) pollution, and (iv) the development of novel procedures for the acquisition of deep sediment cores that are free of microbial contamination from surface soils or other sources.

Studies conducted by several research groups in the early 1980's showed that, despite the common opinion to the contrary, many shallow (less than 30-35 m in depth) subsurface environments, including shallow aquifers, actually contain substantial populations of microbial (mostly bacterial) cells. More recently, it was learned that substantial microbial populations also occur in much deeper aquifers, and it is the research on these deeper aquifers that is discussed in this report.

The research on microorganisms in deep aquifers was part of a new U.S. DOE program on deep subsurface microbiology. In the first phase of this program, three sets of deep sediment cores were obtained (from three separate boreholes, to a depth of 265 m) at the site of DOE's Savannah River Plant (SRP) near Aiken, S.C. At each of the three boreholes, samples were taken from the surface soil, the unsaturated zone above the water table, each of the major aquifers beneath the site, and many of the relatively nontransmissive clay confining layers between the aquifers. All of the samples were taken aseptically (using techniques especially designed for the DOE program) and distributed to a multidisciplinary team of investigators (including microbiologists, chemists, geologists, etc.) for analysis.

Most of the deep SRP sediments contained substantial numbers of viable microorganisms (10^5-10^7 cells/g), enough to exert a very marked influence on groundwater and sediment chemistry if they are metabolically active in situ. The microbial numbers varied from one depth to another, being somewhat lower in the unsaturated zone and much lower in the clay confining layers between the aquifers. In the relatively transmissive, aquifer-associated sediments, however, the numbers of microbes were consistently high and did not decrease with increasing depth (thus implying that substantial microbial communities may also occur at much greater depths). Similarly large numbers of microorganisms have been reported to occur in a variety of shallow aquifers in the United States and Europe.

The deep subsurface microflora at the SRP site was exceedingly diverse. Although predominantly (more than 99%) bacterial in composition, it contained several types of eukaryotic forms, including fungi, protozoa, and algae (that could grow heterotrophically in the dark). The bacterial microflora included most of the known physiological groups of bacteria, thereby indicating that a wide variety of physiological processes (i.e., microbially mediated chemical transformations) could occur in the deep aquifers at the SRP site, depending on which members of the microflora were stimulated by the prevailing environmental conditions at any given time. Most of the deep aquifer bacteria were aerobic chemoheterotrophs (bacteria that require molecular oxygen and utilize organic compounds as carbon sources), but there was a considerable amount of diversity within this group of organisms (20-30 different types being present in most aquifer sediments). Some, but not all, of the shallow aquifer sediments examined to date contained a similarly diverse microflora.

Roughly 75% of the chemoheterotrophic bacteria in the SRP deep sediments had physiological traits similar to those of pseudomonads, a group of bacteria known for their ability to oxidize a wide range of complex organic compounds. Although these bacteria must grow quite slowly in situ (owing to the low concentrations of nutrients that prevail in their environment), they were capable of rapid growth and vigorous metabolic activity when stimulated in the laboratory. Such findings imply that subsurface microorganisms may be made to play a significant role in the remediation of contaminated aquifers and other deep subsurface environments (a process commonly called bioremediation). Possible approaches might include the direct stimulation of the in situ microflora (by addition of nutrients, etc.) or the introduction of subsurface microbial isolates that have been genetically engineered to degrade organic contaminants.

Bacteria isolated from deep aquifers at the SRP site ranged from 0.5 to 1.5 μm in diameter and from 1.5 to more than 5.0 μm in length when grown on typical laboratory media. Cell shapes ranged from spheres to long filaments. Direct microscopic observations indicated that the deep aquifer bacteria were smaller in situ (0.3-0.5 μm in diameter; 0.5-1.2 μm in length), probably as a result of the relatively low nutrient levels in their environment. Most of cells were spherical or oval in shape; cylindrical or filamentous cells were seen only rarely. Many deep aquifer bacteria could produce an extracellular slime layer (or "glycocalyx") composed of polysaccharide. These slime layers are thought to enable subsurface bacteria to scavenge nutrients from groundwater and to attach themselves to solid surfaces in aquifer sediments.

Preliminary experiments with a deep aquifer sample (from 200 m below the surface) from the SRP site indicated that at least 96% of the bacteria in this sediment were attached to sediment particles, rather than living freely in the groundwater. Examination of morphological traits indicated that the apparent free-living and attached microbial forms were different. These results imply that (i) only a small proportion of the deep aquifer microflora resides (in a free-living form) in the groundwater and (ii) the organisms that are found in the groundwater are not representative of the larger microbial community that resides in the sediments. Two recent studies involving shallow aquifer sites in Germany, in which the microorganisms in well water and sediments from the aquifer microbial communities probably cannot be sampled adequately by examination of well water from the sites of interest.

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INFORMATION ON DOE'S DEEP MICROBIOLOGY PROGRAM

Program documents, a list of the current investigators, and other information on DOE's new deep microbiology program can be obtained from the program director:

Dr. Frank J. Wobber
U. S. Dept of Energy
Office of Energy Research (ER-75)
Washington, D.C. 20545
301/353-5549

An special issue of Geomicrobiology Journal that will consist of papers describing DOE's deep microbiology research at the Savannah River Plant site is scheduled for publication in 1989. Preprints of these papers can be obtained from most of the current DOE program investigators.

IN SITU SAMPLING OF GROUNDWATER COLLOIDS BY ULTRAFILTRATION PRIOR TO CHARACTERIZATION

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The Paul Scherrer Institute (PSI) scheme of deep groundwater colloid sampling and characterisation is based on the separation of colloids by cross-flow filtration followed by their determination using microbeam techniques (SEM, ESCA, LAMMA) or direct investigation on the membrane (alpha-gamma spectrometry, gravimetry). This is followed by water, filtrate or colloidal concentrate analysis (ICP/AAS, TOC)(1).

While the colloid characterisation must be carried out in the laboratory, the separation step can be carried out either in the laboratory, after transfer of water samples from the site, or on site after transfer of the water from depth to the surface or even in situ.

At PSI, the separation work is performed on site by pulsed diaultrafiltration apparatus (PDUF). In addition, an ultrafiltration probe has been developed for the separation work in situ at depths on up to 1500m. The PDUF has now been used for over two years to qualify the concentration of colloids in granitic groundwater flowing in a fracture (which has been selected for radionuclide migration experiments) in the underground laboratory of the Grimsel Test Site, Switzerland (2). The colloid (40-1000nm size range) concentration in the groundwater of this 500m deep sub-surface system shows no seasonal variation and is constant at about 10^{10} particles per liter (corresponding to about 100ppb).

Since the extraction of water from bore-holes followed by the transfer of water sample from the site to the laboratory alters the characteristics of the colloidal phase, an ultrafiltration probe has been developed to separate the colloids in situ.

The technical details of the probe include:

- SIZE:
  length:160.00 cm
  diameter: 3.20 cm
  membrane diameter: 2.05 cm

- LIMITATIONS:
  T(max) 75 C
  P(max) 150 bar
  V(max) 195 ml
  Working depth: 1500 m

The final goal of this study is the production of accurate data on colloidal concentrations and characteristics from sub-surface systems relevant to radwaste repository safety assessment programmes.

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COLLOIDAL CONSIDERATIONS IN SAMPLING GROUND WATER FOR INORGANICS PINAL CREEK, GLOBE, ARIZONA

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The association of contaminants with suspended colloidal material in ground water is a possible transport mechanism and a complicating factor for accurate geochemical estimations. Analytical methods to determine "dissolved" metal concentrations have historically used 0.45 micron (μm) filters to separate dissolved and particulate phases. Colloids with sorbed toxic metals may either by larger or smaller than 0.45 μm. If the determination is an evaluation of 'mobile' species in solution, significant underestimations may result, due to colloidal associations. On the other hand, if filtration is used to determine truly dissolved aqueous species, the passage of colloidal material less than 0.45 um in size may result in overestimation of dissolved concentrations.

A study was initiated at Pinal Creek, Arizona to characterize this component of transport at the site and also investigate the appropriateness and practicality of recently recommended sampling procedures for metals in ground waters given concerns about colloidal mobility (1). A brief summary of those recommendations were to:

1) isolate the sampling zone to minimize aeration and mixing of distinct geochemical zones,
2) use low flow rate pumping (as close to ground water flow velocity as possible) in well purging and collection of samples,
3) monitor ground water parameters during purging and sampling for indication of when to initiate sample collection, and
4) collection of both filtered and unfiltered samples.

Pinal Creek is an active copper mining area where acidic wastes have leached into the ground water resulting in an extensive contaminant plume extending about 16 km (2, 3,). Study techniques included multiple filtrations in the field in air and under nitrogen, particle size and intensity analyses with a laser light scattering instrument during well purging and sample collection, elemental analyses of filtrates using inductively coupled argon plasma (ICP), atomic absorption with graphite furnace (AAGF), and ion chromatography, and filter analyses by scanning electron microscopy(SEM).

Isolation of the sampling zone--This was accomplished using a packer arrangement in the wells. The packer was inflated with nitrogen and permitted the purging of a smaller volume of water prior to initiation of sampling. In addition, aeration of the sample was minimized and mixing between distinctly different geochemical ground water zones was avoided. Significant differences in major cation chemistry were observed in one well (X1W5) in the conglomerate when the packer was not used.

Monitoring Water Parameters During Purging and Sampling--Monitoring of dissolved oxygen, temperature, conductivity, pH, redox and turbidity during well purging was performed to determine when to begin sampling based on the stability of ground water quality conditions. Measurements were taken with a Hydrolab Surveyor 2 multiparameter field meter equipped with a flow-through cell. A Malvern Multisizer II was used throughout the purging to determine particle counts and size distributions. Particle counts were the slowest to stabilize, consistently requiring about twice as long as the other parameters. In terms of acquiring samples representative of naturally suspended particulates for contaminant transport considerations, this was the most important parameter to monitor.

Low flow rate pumping--A small diameter bladder pump (0.6-1.0 L/min), a low speed submersible pump (3.8 L/min) and a high speed submersible pump (100 L/min) were used to collect ground water samples. While not always possible, the goal is to pump the well at approximately the same rate as the ground water flow velocity past the screened interval in the well. In the alluvium, the estimated ground water flow velocity was estimated at about 1 L/min, while in the conglomerate it was considerable slower. In all wells sampled, it took longer for the bladder pump to reach steady-state values for monitored constituents, but particle counts and particle size distributions were lower throughout pumping. It was obvious from particle counts, size distributions and SEM filter analyses that the higher speed pumps created significant disturbance, as evidenced by the rise in particle counts, especially with the 100 L/min submersible pump.

Estimates of stable suspended particle concentrations were achieved with the laser light scattering instrument and calibration curves constructed using particles similar to those identified on the filters with SEM. In one well (451), concentrations of suspended particles were as high as 28 ppm.

Collection of Filtered and Unfiltered Samples--Samples were collected both in air and under nitrogen using a field glove box. Unfiltered and filtered samples were collected using Millipore and Nucleopore filters ranging in pore size from 0.03 to 10.0 microns. Well X3W3 showed consistently increasing concentrations (>10%) of most inorganic elements with increasing filter pore size. Filtrate differences for well X5W3 were significantly higher for concentrations of aluminum, iron and potassium with increasing filter pore size. This was explained by SEM analyses of filters from this well which showed kaolinate to be the predominant retained particle, with many of the particles having significant iron coatings.

Differences in elemental concentrations between samples collected under nitrogen and in air were observed in sell X3W3 for iron, Manganese, nickel, zinc and lead. Even with immediate acidification, there was apparently some oxidation of iron prior to analysis in the samples not collected under N_2.

Conclusions-- While differences in elemental concentrations using different filter pore sizes were not dramatic, trends showing increasing concentrations with increasing filter size in several of the wells were observed. High speed submersible pumps greatly agitate the sampling zone, causing entrainment of normally non-mobile particles. Monitoring of turbidity, along with other parameters such as dissolved oxygen, conductivity, temperature, and pH is recommended prior to sampling. Collection of samples under nitrogen is recommended for anoxic waters, and given the present uncertainty concerning colloidal transport, use of filters larger than 0.45 μm is suggested for accurate estimations of mobile contaminant loading. Use of smaller (e.g. 0.10 μm) pore size filters may be appropriate for estimating truly dissolved concentrations.

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EFFECT OF COLLOIDS ON ACTINIDE MOBILITY IN SURFACE WATERS

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Hollow fiber diafiltration (HFD) has been used to separate natural colloids on the basis of size. HFD has the advantages of reproducibility and of being suitable for large sample sizes. Water samples of hundreds of liters can be concentrated to a small volume so that even dilute colloids can be brought within reach of conventional analytical techniques. This approach has been applied to the study of colloid properties in two lakes contaminated with actinides. Principal findings can be itemized as follows:

1. Of the actinides in the conventional "dissolved" phase (less than 0.45 micron), more than 90% are found to be associated with colloids larger than 1.5 nm in size. Given the errors of analysis, it is possible to conjecture that there may be no such thing as truly dissolved Th(IV), Am(III), or Pu(IV). Using the 1.5 nm size as an arbitrary breakpoint between bound and free adsorbate, binding coefficients are at least 20 times greater than the conventionally-measured K_D would indicate.

2. The binding of actinides to those colloid fractions is reversible. If different isotopes of Pu, Th, Am and Cm are added to filtered lake waters, these come into equilibrium with the ambient isotopes in individual HFD fractions generally within a day.

3. Plutonium in its two normal ambient oxidation states, (IV) and (V), can be separated by HFD. Pu(IV), which is strongly surface-reactive, was progressively removed by smaller hollow-fiber filters, while Pu(V), which is not surface-reactive, was not removed by the smallest filter.

4. Attempts to correlate gross composition of particulate fractions with actinide binding fails to support the hypotheses that binding properties are controlled by either iron or organic carbon.

5. There is no evidence for coagulation of concentrated colloids, at least across the 2.5 nm size boundary. If the colloids were coagulating, the colloid population would tend to shift from small colloids to larger as a sample was concentrated. The proportion of colloids less than 2.5 nm would be expected to decrease, and they would carry a smaller proportion of the actinides through the filter. Instead, what is observed is that a sample is concentrated by HFD, the concentration of plutonium and americium in the dialysate <u>increases</u> slightly (about a 25% increase after a 5-fold concentration). This could be "explained" by the particle concentration effect.

Collaborators in this work are Kent Orlandini (Argonne), John Pinder, and John Bowling (Savannah River Ecology Laboratory), and Bernard Harvey and Brian Lovett (Ministry of Agriculture, Fisheries, and Food, Lowestoft, United Kingdom). Our portion of the research was supported by the DOE Office of Health and Environmental Research.

SESSION II.

CHEMICAL AND HYDROLOGIC FACTORS CONTROLLING COLLOID TRANSPORT

Moderated by John F. McCarthy [ORNL]

Objective of the Session: To critically review observations of colloid movement in laboratory and field systems, with an emphasis on the chemical and hydrological factors controlling transport.

Titles and Authors of Platform Presentations:

Movement of Colloidal Particles in Saturated Media at The Chalk River Nuclear Research Laboratory
D. R. Champ [Chalk River Nuclear Research Laboratory]

Colloid-Facilitated Transport in Groundwater: Laboratory and Field Observations
B. B. Looney [Savannah River Ecology Laboratory], M. E. Newman, and A. W. Elzerman [Clemson University]

Formation and Mobilization of Colloidal Particles in Contaminant Plumes
P. M. Gschwend [MIT]

Chemical and Hydrologic Factors Controlling the Transport of Organic Colloids
P. M. Jardine, N. Weber, and J. F. McCarthy [ORNL]

Transport of Organic Macromolecules in Porous Media
C. G. Enfield [U.S. Environmental Protection Agency]

Mobility of Microorganisms in Porous Media
R. W. Harvey [U.S. Geological Survey]

Observations in Biocolloid Transport in Saturated Systems
C. Gerba and R. Bales [University of Arizona]

Fluid Mechanical Considerations on Colloidal Transport in Porous Media
P. F. Germann [Rutgers University]

Colloidally Induced Fines Migration in Porous Media
H. S. Fogler [University of Michigan]

Titles and Authors of Poster Presentations:

Coagulation of Colloidal Iron Oxide Particles in Water: Surface Chemistry, Electrokinetics and Dynamic Stability
L. Liang and J. J. Morgan [California Institute of Technology]

Degradation and Partitioning of Naphthalene in Soil
A. I. Ononye, J. D. Wolt, and J. G. Graveel [University of Tennessee]

Partitioning Behavior of Groundwater Bacteria
R. Lindquist and G. Bengstsson [University of Lund]

Transport and Retention of Microspheres and Dissolved Organic Carbon in Sand Columns
L. E. Toran, A. V. Palumbo, and J. F. McCarthy [ORNL]

OBSERVATIONS ON THE MOVEMENT OF COLLOIDAL PARTICLES IN SATURATED MEDIA AT THE CHALK RIVER NUCLEAR LABORATORIES

D. R. Champ
Chalk River Nuclear Laboratories, Canada

The transport of particles or colloids in groundwater flow systems has been a major interest in my laboratory since the late 1970's. The interest was triggered primarily by observations made at the Chalk River Nuclear Laboratories (CRNL) Glass Block site. The subsequent studies, some of which are described below, have encompassed both inorganic contaminants and microorganisms. The results have shown that the transport of particles or colloids may be significant for some contaminants in some groundwater flow systems.

In June 1960 twenty-five nepheline syenite-based glass hemispheres containing the fission products ^{137}Cs, ^{90}Sr, ^{144}Ce and ^{106}Ru were buried below the water table in sandy soil at the Chalk River Nuclear Laboratories (1). Subsequently field measurements were made of the distribution of leached fission products in the soil and water downgradient of the blocks. Comparison of the field observations with model predictions for ^{137}Cs showed a considerable deviation from an idealized cation exchange equilibrium process (2). One hypothesis for the behavior of the ^{137}Cs was migration of the radionuclide as, or in association with, fine particles or colloids. This hypothesis was tested by preparing soil columns from cores recovered from the Glass Block site, spiking them with 3.7 x 10^7 Bq of ^{134}Cs, eluting with groundwater from the field site, and measuring ^{134}Cs in the column effluent (3). Low levels of Cs were released continuously from the columns and approximately 85% of the eluted Cs was shown to be associated with particles 0.2 to 1.0 um in size. The release of both the Cs and particles was shown also to be biologically mediated by bacterial species present in the groundwater from the site. These column experiments supported the hypothesis that particulate transport could be an important process affecting the migration of Cs.

Similar conclusions were reached in a laboratory evaluation of the migration of ^{239}Pu through soil columns (4). Soil columns prepared from undisturbed cores from the Glass Block site were loaded with a ^{239}Pu spike in the feedwater, and eluted with groundwater. The release of Pu was followed with and without temperature or antibiotic manipulation of the columns. Small amounts of Pu were continuously released from the columns, and at steady state, approximately 50% was associated with particulates (retained on 0.45 um filters). More detailed analyses of the size distribution of the Pu in the groundwater effluent indicated further that a significant proportion

(>25%) of the Pu could also be classified as colloidal. Manipulation of the columns with temperature cycling or antibiotics resulted in significant decreases in the release rate of the Pu. In both cases the decrease in the release rate of particulate forms was significantly greater than that for the dissolved forms. From these results we concluded that bacterial involvement in the transport of Pu in association with particles was highly probable.

Field confirmation of the presence of particulate forms of these and other radionuclides in the groundwater flow systems at Chalk River was achieved in a program to examine the chemical speciation of radionuclides in contaminant plumes at CRNL (5). Four contaminant plumes, including the plume downgradient of the Glass Block site, were sampled with a large volume water sampler that facilitated the identification of particulate as well as anionic, cationic and non-ionic species. Particulate forms were observed for most radionuclides, although the percentage was very low for some. Isotopes of cesium were most frequently associated with particulates as evidence by the large percentage (4.2 to 86%) in particulate form in the various plumes and sampling locations. Data from the Glass Block site suggested that particulate forms of cesium may be released from the blocks themselves and then undergo removal by filtration or degradation to a form that can be sorbed. Data from all other sites that involved only liquid disposals supports the in-situ production of the particulate cesium. For Pu, 1% or less of the activity was associated with particles >0.4 um in size. Nevertheless, the data support particulate transport of Pu over distances of 10's to 100's of meters.

The followup speciation studies to determine the composition of the <0.45 um fraction in more detail have not yet been undertaken. A current study using core columns in-situ, however, should provide data relevant to the natural groundwater environment. In this work an in-situ field column technique described by Champ et al. (6) is being applied to assess the transport of radioisotopes with long half-lives (I, Tc, Pu, Am and Np) in overburden sediments. A field site located adjacent to the Ottawa River was developed and is being used in this work. The Ottawa River is the regional low for this area; the river and adjacent land are likely points for discharge of deep waters. The field column experiments are being performed at the base of the overburden sequence in a zone of probably discharge from the bedrock. In the first phase of work we studied the transport of I and Tc (plus Sr as a reference reactive radioisotope). In the second phase we are addressing these radioisotopes in more detail as well as Pu, Am, and Np.

The occurrence and movement of microorganisms in groundwater systems has been a topic of increasing interest in contaminant hydrogeology, partly because of the potential for mediation of the transport of various contaminants (7), but also by virtue of the directly detrimental impact that their presence may have. Recently the potential for transport and survival of bacteria in fractured crystalline rock was assessed in a series of field scale tracer tests at our laboratories (8). In these experiments the breakthrough curves for injected Escherichia coli and non-reactive particle tracers (polystyrene beads) were compared with those for conservative inorganic and radioactive tracers. Rapid transport, relative to the conservative tracers, of both bacteria and non- reactive particles were observed. The first appearance of both was with, or slightly before, the first arrival of the conservative dissolved tracers. Removal of the bacteria nd particles by filtration processes occurred and was quantified through the calculation of filter factors. The filtration process in our fracture system was similar to that found in a gravel aquifer. From the results we concluded that particulate contaminants can be very rapidly transported in fracture systems and that continuing sources of contamination could lead to relatively high local concentrations of particulate contaminants compared with the average at any given distance from the source. It was also concluded that using traditional conservative tracers of water movement to assess the potential for movement of particulate contaminants could lead to significant underestimates of exposure to particulate contaminants when water from water supply wells is located in fractured media.

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COLLOID FACILITATED TRANSPORT IN GROUNDWATER: LABORATORY AND FIELD STUDIES

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Several factors may enhance the mobility of chemicals in subsurface systems. Waste constituents may exist in the "free" or aquated form or they may associate with a variety of alternate phases, such as inorganic ligands, organic ligands, or colloids in these systems. Complexation or sorption of a fraction of the mass of a waste constituent to these alternate phases may result in mobility in excess of that predicted using a single K_d value derived from simpler systems. The enhanced mobility, or facilitated transport, that results from these varied and complex processes must be incorporated into waste site assessment models to allow reasonable estimations of risk to be made. A simple empirical approach to account for facilitated transport was developed to support risk assessment modeling of waste sites at the Savannah River Plant in Aiken SC. A research program was initiated to more fully evaluate the facilitated transport process based on laboratory studies, theoretical calculations and field investigations. A review of the original field observations, the empirical approach developed, laboratory column studies, geochemical speciation models, and carefully collected field samples provide compelling evidence related to facilitated transport in general, and the role of colloids in enhancing waste migration in particular.

Background -- The Savannah River Plant (SRP) is a nuclear production facility operated for the U.S. Department of Energy by E. I. du Point de Nemours and Company. Recently, detailed environmental assessments for forty-eight locations that received (or may have received) a variety of radioactive and nonradioactive constituents during the past 35 years were completed and documented. These assessments included an estimation of risk, or residual risk, posed by each disposal area to various receptors as a function of waste management action. Modeling of chemical transport in the subsurface was an integral part of the assessment process. The performance of the subsurface transport models was evaluated by peer review, comparison with alternate modeling approaches, and comparison of predictions to field observations. The evaluation of model performance with respect to field observations led to the development of an empirical approach to incorporate colloid/chemical facilitated transport in a straightforward manner. A summary of the subsurface model quality assurance report stated:

> *"In general, the various evaluations suggested that the selected model (1-D advection with longitudinal dispersion and decoupled transverse dispersion) was a reasonable screening tool. Specifically, the results suggest that chemical speciation must be addressed to predict measured concentrations adequately...."*

A simple approach was developed to account for the facilitated transport that results from association of waste constituents with alternate phases or from changes in bulk chemistry within the plume. A facilitated transport fraction (FTF) was used to estimate the portion of the total disposed mass for each constituent that is subject to enhance mobility. This approach was carried out by: (1) determining FTF values for each constituent based on monitoring data at a well characterized site, (2) applying the FTF values to the appropriate constituent(s) at each site to determine a mobile fraction and a fraction that is assumed to behave according to standard K_d formulations, and (3) using the resulting source information to carry out the environmental assessment using a K_d of 0.001 for the mobile fraction.

FTF values were derived using data from the M-Area Settling Basin and the Radioactive Waste Burial Grounds. FTF values were generated for all constituents that are theoretically sequestered in the vadose zone, but were measured in the groundwater. In each case, the FTF for an element was derived based on the assumption that the downgradient groundwater concentration of a conservative tracer is related to source strength in a fashion similar to the element's mobile fraction. The resulting FTF values ranged from << 0.0001 to 0.04; specific elements were grouped as follows:

FTF range: << 0.0001 to <0.001 Elements: Cesium, Cobalt, Strontium, Plutonium

FTF range: 0.001 to <0.01 Elements:Barium, Cadmium, Chronmium, Mercury, Nickel, Uranium

FTF range: > 0.01 to 0.04 Elements: Copper, Lead, Silver.

The FTF values estimated from large well-characterized waste areas are likely to represent maximum enhanced transport due to the relatively abundant ligands and colloids present during site operation or due to colloids generated by altering the solution chemistry in the subsurface matrix.

While this "worst case" calculation is adequate to meet some assessment needs, facilitated transport at small waste disposal sites and from spill sites will be dominated by more dilute solutions and mobile colloids that are present at ambient levels. As a result of the expected variations in waste migration at the variety of potential waste sites, a research program to more fully evaluate subsurface transport and to develop more robust models for future risk assessments was initiated.

Laboratory Studies -- The laboratory studies and theoretical modeling were designed to provide insight into facilitated transport under a range of conditions:

Scenario 1 - Pulse input of contaminant to a subsurface system. This is equivalent to a spill of waste followed by leaching with rainfall. The facilitated transport in such a system can generally be attributed to colloids and will be minimally the result of plume chemistry (e.g., major cations and anions, alteration of the solid surfaced, or generation of colloids due to interaction of the solid matrix with the plume).

Scenario 2 - Landfill or Shallow Land Burial. This type of system is characterized by a decreasing release over time from the solid waste forms. Both chemical and colloidal mechanisms of facilitated transport are potentially significant in this situation.

Scenario 3 - Seepage from a Waste Basin. This type of system is characterized by large volumes of relatively concentrated waste entering the subsurface. The resulting major shifts in water chemistry maximize the importance of chemical mechanisms in facilitating transport.

Column experiments to replicate Scenarios 1 and 3 were carried out (the behavior of Scenario 2 would fall between these end members).

The column experiments were carried out using 18 cm x 1.5 cm polyethylene columns that were prepared by roughing the inside surface with sandpaper and caped with 1 cam glass wool plugs and end caps. The various scenarios approximated using simulated waste and rain as appropriate. Several conclusions related to the Scenario 1 (pulse input) experiments are apparent:

(1) The eluent from the column of packed soil is highly variable. Bulk parameters (such as pH, specific conductance, and turbidity), as well as specific components show the variability.

(2) Elution from "blank" columns was also highly variable (in some cases showing relatively high concentrations of specific elements).

(3) Elution of colloidal material from the columns was a common and important factor.

(4) Relatively mobile major ions (e.g. Cl and NO_3) were collected in the early fractions.

(5) Specific metals behaved differently in columns receiving different pH waste (e.g., Pb and Cd appear more mobile in acidic vs basic pH waste systems).

(6) The soil columns sequestered most of the trace metals applied even though peaks in concentration were measured in the column effluent (i.e., only a small fraction of the mass applied was recovered).

Several additional conclusions related to the Scenario 3 (step input) experiments are apparent:

(1) Most constituents were more mobile in the acidic wastes than in the basic wastes. Cr was an exception.

(2) There was a good recovery of many of the trace metals in the column effluent of the acidic waste column. Cr was an exception.

(3) Cr was mobile and well recovered in the column receiving basic wastes.

(4) Much of the transport appears to be related to chemical factors (e.g., exhausting neutralizing capacity of the soil) in the columns receiving acidic wastes. The columns receiving basic wastes were highly variable and similar to the pulse input. Colloids may play a role in both systems.

(5) Most elements behaved similarly in a complex waste solution and as a component in a simple pH adjusted solution. Pb was an exception; the presence of high NO_3, Na, etc. appear to enhance the migration of Pb relative to the other trace metals.

Colloidal material eluted from the columns was analyzed using SEM/XRF and the particles appear to be primarily clay minerals.

Field Studies -- Leachate was collected from a large reconstructed soil profile that has been fitted with a leachate collection system. The profiles have been in place for over two years so that the original disturbance should have minimal effects on the current leachate; also, the leachate passes through the soil at normal field velocities. Leachate was analyzed by SEM/XRF and the results suggest important similarities and differences relative to the lab columns. In the field studies, a large number of the particles appear to be organic in nature. The inorganic particles are primarily clay minerals. In both the laboratory and field studies the particles were primarily silica and aluminum based on with lower concentrations of iron and other elements. In the column studies, measurable levels of waste constituents were observed on the eluting particles.

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FORMATION AND MOBILIZATION OF COLLOIDAL PARTICLES IN CONTAMINANT PLUMES

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To ascertain why colloids occur in some groundwater, we have investigated the types of microparticles present at various sites (New Jersey, Delaware, and Nevada). At two mid-Atlantic sites, kaolinitic clays predominated in groundwater suspensions (~10 -100 mg/L) where conditions have lead to the absence of dissolved oxygen. SEM-EDAX observations show some iron oxides are associated with these clays. By comparison to neighboring sites which exhibit rust-colored aquifer solids, we have deduced that introduction of organic matter via recharging waters has caused these subsurface systems to go locally reducing. In response, iron oxide phases, previously serving as secondary cements coupling soil clays to the predominantly quartzitic aquifer solids, have begun to dissolve and thereby free the clays to be carried away in groundwater suspensions. Some organic coatings may also be covering iron oxide particles in the suspension and remaining as coatings on immobile quartz grains, thereby promoting colloid stability. At the western location, silicate colloids were found at approximately 10 - 100 mg/L in well waters recharged through fly ashes. Groundwater containing these microparticles were especially enriched in pCO_2 as compared to neighboring sites without colloids. Examination of the soil and groundwater chemistry suggests these colloids were mobilized due to infiltrating waters building up CO_2 (possibly in response to oxidation of organic matter), which subsequently caused the dissolution of secondary carbonate solids. If such carbonated were acting to cement the soil silicate colloids to the predominantly quartz media, then their dissolution would allow the colloidal mobilization. These site studies indicate that soil colloids may be mobilized where recharging fluids can upset processes binding soil particles together, e.g., secondary cementation. Such mobilization can have impacts on subsurface permeability, both increasing it at points and decreasing it where colloids re-attach. Also, since colloidal phases frequently provide much of the sorption sites retarding subsurface chemical transport, their mobilization can both lower the affinity of pollutants to the immobile phases and enhance the ability of the mobile media for carrying contaminants.

CHEMICAL AND HYDROLOGIC FACTORS CONTROLLING THE TRANSPORT OF ORGANIC COLLOIDS

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The subsurface transport of inorganic and organic contaminants may be strongly related to the movement of colloidal organic matter (COM) through a soil profile. Understanding the transport characteristics of COM in porous media will assist in predicting the movement of contaminants within and away from DOE sites.

The chemical and hydrologic factors controlling the subsurface transport of COM through a proposed waste site on the Walker Branch watershed in eastern Tennessee was investigated. Field experiments were conducted on an undisturbed soil pedon (2m X 2m X 3m deep) which was isolated on a ridgetop site (1). The soil pedon has been instrumented with fritted glass solution samplers and tensiometers inserted laterally within the soil at nine depths. The mobility of inorganic and natural COM tracers added to the pedon surface were monitored with time and depth. Laboratory studies designed to compliment the field study, utilized a batch technique to investigate the sources of COM adsorption in the soil and the chemical mechanisms operative during the adsorption process (2).

Both field and laboratory analysis indicated that COM adsorption increased with increasing soil depth which was related to the quantity and type of mineralogy present as well as the indigenous organic carbon content. Large amounts of indigenous soil organic matter tended to impede the adsorption of added COM. Both crystalline and noncrystalline Fe-oxides and hydroxides from the soil retained ≈50 % of the total adsorbed COM. Phyllosilicates in the <2um clay fraction adsorbed the remaining COM with kaolinite exhibiting the largest adsorption capacity.

Both field and laboratory studies suggested that the hydrophobic COM fraction was preferentially adsorbed by the soil relative to the hydrophilic fraction, with the adsorption of the hydrophobic acid component increasing with profile depth. Organic contaminants have been shown to associate primarily with the hydrophobic fraction of COM. Since this fraction is preferentially adsorbed by soil, the impeded transport of colloid associated contaminants in soil might be expected.

The primary adsorption mechanism of these organic solutes to soil is believed to be physical adsorption driven by favorable entropy changes. An anion exchange mechanism accounts for the remaining adsorbed DOC, which is ≈25 % of the total attenuated DOC. For this soil, the contribution of ligand exchange was minimal as determined from thermodynamic principles.

Field studies stressed that although COM is a highly reactive constituent in these soils, its mobility through the profile is largely controlled by preferential flow processes. The transport of COM is strongly dependent on the duration and intensity of rainfall, with certain storm events channeling all forms of COM deep into the soil profile.

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CHEMICAL TRANSPORT FACILITATED BY COLLOIDAL-SIZED ORGANIC MOLECULES

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The fluid passing through the pores of soils and geologic materials is not just water with dissolved inorganic chemicals but a complex mixture of organic and inorganic molecules. Large organic molecules such as humic and fulvic materials may impact the movement of contaminants. If the large organic molecules are mobile and they act lake surfactant micelles, they can facilitate the movement of hydrophobic organic contaminants. Enfield and Bengtsson (1) performed a sensitivity analysis evaluating the importance of several processes that might impact the movement of hydrophobic organic chemicals. They developed a transport equation

$$\frac{\partial(\theta\rho_a C_a)}{\partial t} + \frac{\partial(\phi\rho_o C_o)}{\partial t} + \frac{\partial[(1-n)\rho_s C_s]}{\partial t} = D_a \frac{\partial^2(\theta\rho_a C_a)}{\partial x^2}$$

$$+ D_o \frac{\partial^2(\phi\rho_o C_o)}{\partial x^2} - V_a \frac{\partial(\theta\rho_a C_a)}{\partial x} - V_o \frac{\partial(\phi\rho_o C_o)}{\partial x} \qquad (1)$$

by assuming local equilibrium they were able to solve Eq. 1 as:

$$R^* \frac{\partial C^*}{\partial t} = D^* \frac{\partial^2 C^*}{\partial x^2} - V^* \frac{\partial C^*}{\partial x} \qquad (2)$$

where

$$R^* = 1 + \frac{(1-n)\rho_s}{\theta\rho_a} k_d + \frac{\phi\rho_a}{\theta\rho_a} k_p \qquad (3)$$

$$D^* = D_a + \frac{\phi\rho_a}{\theta\rho_a} k_p D_o \qquad (4)$$

$$V^* = V_a + \frac{\phi\rho_a}{\theta\rho_a} k_p V_o \qquad (5)$$

The sensitivity shown in these analysis demonstrate the importance of a knowledge of the mobility of the organic colloids and the ability of the organic colloids to partition a contaminant and facilitate its movement as well as the amount of organic colloid present. The analysis indicate that if the colloid is not mobile it will not have an impact on chemical transport. As yet, little work has been completed on the mobility of organic colloids in natural environments and only limited work has been conducted under laboratory conditions. Large organic complexes such as bacteria, virus, and humates and fulvates are found in most ground waters but little is known about their mobility. The more hydrophilic the organic material, the more likely it is to be mobile. Simultaneously, the more hydrophilic the material, the less likely it is to "sorb" a hydrophobic contaminant. This analysis also shows the importance of the amount of mobile carbon assuming the partition coefficient was the same for all carbon (mobile and associated with the mineral fraction of the soil).

Bengtsson et al. (2) presented experimental evidence of facilitated transport for hexachlorobenzene due to the presence of a polysaccharide (blue dextran). Blue dextran was shown to move through the soil faster than the average velocity of water. The accelerated movement of the blue dextran with respect to water was attributed to the size of the blue dextran molecule. The large blue dextran molecule was assumed to be excluded from the smaller pores in the soil, thereby reducing the void volume accessible to the blue dextran. Even though the blue dextran was extremely hydrophilic, it still had a significant blue dextran:water partition coefficient and significantly increased the mobility of the hexachlorobenzene.

From the described sensitivity analysis, it appears that colloidal-sized organic molecules will have a significant impact on the transport of hydrophobic chemicals with log K_{OW} greater than three and if the organic colloid:water partition coefficient is approximately the same as or greater than the soil organic carbon:water partition coefficient. Facilitated transport will be an effective mechanism in cases where the fluid moving in the pores contains 10 or more mg carbon/l. Considering the amount of carbon observed in leachates from municipal landfills and other highly contaminated sites, significant facilitated transport of hydrophobic contaminants is possible by this mechanism.

Although the work reported in this abstract was funded in part by the US EPA, it has not been subjected to formal agency review and does not necessarily reflect agency views.

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TRANSPORT OF BACTERIA IN A CONTAMINATED AQUIFER

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Migration of indigenous bacteria through contaminated aquifers is becoming an increasingly important issue in waste management. Degradation of highly mobile and persistent ground water contaminants may be enhanced by contransport of bacteria that have become acclimated to their degradation. Transport of nonindigenous bacteria in ground water also is of environmental concern, inasmuch as the appearance of microbial pathogens in water-supply wells has contributed significantly to the number of waterborne disease outbreaks (1). Also, the success of many schemes that employ genetic technology in-situ treatment of organically contaminated aquifers depends upon the ability of the engineered organism to reach the contaminant-affected area in the aquifer. Some models can predict the extent of transport of bacteria through porous media (2, 3); however, these models can substantially underestimate bacterial transport that is observed in the field (4) and corroborative experimental data on bacterial transport are scarce. It is clear that improvements to models and additional experimental data on bacterial transport are needed to predict the movement of indigenous and nonindigenous bacteria through porous-media aquifers. Two factors are evaluated here: (1) the importance of colloid filtration theory as a major determinant of the extent of transport and the size distribution of transported bacteria in the contaminant plume, and (2) the importance of secondary pore structure (macropores) to the transport of bacteria through sandy aquifer sediments.

Small-scale, natural-gradient tests with stained bacteria and bromide were conducted in an area of organically contaminated ground water described in earlier microbiological studies (5, 6; Cape Cod, Massachusetts) and in the lab, by use of flow-through columns packed with aquifer sediments. In the small-scale injection experiments, the arrival time downgradient of the stained bacteria was nearly coincident with that of Br^-. In contrast, calculated retardation factors (RF) (ratio of time required to reach peak abundance for the microorganisms to time to peak concentration for Br^-) for injection tests employed in other aquifers are often substantially less than 1.0. However, a RF less than 1.0 at a point 3.2 m downgradient was obtained in a previous forced-gradient experiment with stained indigenous bacteria that was done at another site in the Cape Cod aquifer. Retardation factors substantially less than 1.0 indicate that transport of microorganisms not attenuated by the medium is, on the average, significantly faster than that of Br^- and, presumably, mean ground water flow. The apparent enhancement in transport velocity of the unattenuated microorganisms appears to be greatest in tracer experiments involving fractured aquifers. It is hypothesized that this phenomenon is caused by preferential transport of the microbes along preferred flow paths (large pores and channels) because they may be excluded from the smaller pores on the basis of size. The near absence of rapid transport of the indigenous bacteria relative to Br^- in the small-scale, natural-gradient tests at the Cape Code site may be caused by the absence of much secondary pore structure; this is consistent with the tightly packed, well-sorted nature of the aquifer sediments.

Inasmuch as the colloid-filtration model predicts differential transport on the basis of particle size (7), a dispersion-corrected colloid filtration model was applied to observed size distributions of the free-living bacterial population in contaminated ground water adjacent to the sewage-infiltration beds. The objective was to compare predicted size distributions with observed values at various distances downgradient. Because alpha may differ spatially, a range of estimates were used in this model. An alpha value of 10^{-4}, which falls within the range of estimates calculated in this study resulted in predicted size distributions for unattached bacteria that were quite similar to those that were observed, particularly in ground water 0.65 km downgradient (8).

The observed and predicted decreases in average cell size with increasing distance downgradient from the source of contamination is not what would be predicted on the basis of nutrient availability. This is because average cell size commonly is directly related to nutrient content of the environment. Therefore, free-living bacteria in high-nutrient ground water close to the sewage loading beds may be expected to have a larger average cell size than bacteria in nutrient-depleted ground water further downgradient. It is possible that the observed changes in cell-size distribution is a result of the shift in the makeup of the bacterial population with increasing distance downgradient. However, substantial increases in average diameter of polydispersed populations of bacteria-sized microspheres have been observed during transport in ground water injection experiments. Therefore, it seems reasonable to invoke an abiotic mechanism, at least in part, to explain observed increases in bacterial size during transport through the aquifer. Because the transport process may depend on the bacterial size class, bacterial size may be a factor to consider in aquifer-restoration experiments in which selected or genetically engineered bacteria are injected into an organic-contaminated ground water.

The importance of secondary pore structure to the transport characteristics of bacteria-sized particles in the Cape Cod aquifer may be examined by employing repacked aquifer sediments in flow-through column experiments. The objective was to alter the secondary pore structure of the aquifer sediments dramatically from what is observed at the field site. Aquifer sediments were collected from the site, sterilized, and repacked into glass columns (0.6 m long, 5.0 cm inside diameter) to examine the effect of secondary pore structure upon transport characteristics of bacteria-sized particles. Well-characterized, bacteria-sized microspheres (carboxylated latex; 0.2 0.7, and 1.35 μm diameter) and Br- (20 mg/L) were added as injectate to the columns. Data on breakthrough of the different sizes of carboxylated microspheres was compared to data generated in a small-scale forced-gradient field test reported earlier (9). Immobilization of microspheres in the column was inversely related to size; that is, the smaller microspheres were attenuated by the media to a lesser degree than the larger microspheres. It is not clear why the smaller microspheres are preferentially transported through the column relative to larger microspheres, although straining may be a possibility. This was in direct contrast to their transport characteristics in the aquifer, where the smaller microspheres were immobilized in aquifer sediments to a greater degree than were the larger microspheres. This observation is consistent with colloid-filtration theory, which predicts that smaller bacteria-sized particles being transported through porous media should become immobilized at stationary solid surfaces faster than larger bacteria-sized particles (7). The reason for this is that fine-scale particle movement, and the likelihood that particles will encounter a solid surface, are governed largely by diffusion or Brownian motion, which increases with decreasing particle size.

In the aquifer material of Cape Cod, the carboxylated microspheres were somewhat retarded relative to Br-, apparently because of their surface characteristics (9). The more rapid transport of the microspheres relative to Br- in the column experiment suggests that substantial secondary pore structure was created when the column was packed with aquifer material or resaturated with water. It has been observed, from previous flow-through column experiments (Harvey, R.W., USGS, unpublished data) that transport characteristics of both bacteria and microspheres is partially dependent on the manner in which the columns are packed. Therefore, transport characteristics of bacteria and bacteria-sized particles through columns that have been repacked with subsurface sediments can be quite complex and it appears that a great deal of caution must be exercised when extrapolating results of particle transport studies performed with columns to the ground water environments.

In summary, there are many factors, both biotic and abiotic, that can affect transport of bacteria through contaminated aquifers. The importance of secondary pore structure and colloid filtration cannot be ignored. Additional data on bacterial transport are needed, preferably from a variety of aquifers and hydrologic conditions.

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OBSERVATIONS IN BIOCOLLOID TRANSPORT IN SATURATED SYSTEMS

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Bacteriophage transport was investigated in laboratory column experiments using sandy soil, a controlled field study in a sandy wash, and laboratory experiments using fractured rock. Results illustrate the inability of a solute tracer to provide estimates for dispersion and effective porosity that apply to a colloid (1). Bacteriophage can be used to better estimate the maximum subsurface transport rate of colloidal contaminants through a porous formation. In the media studied, the bacteriophage MS-2 and f2 acted as conservative traceries, i.e. they did not adhere to the aquifer media.

In the soil columns the phage MS-2 exhibited significant dispersion and was excluded from 35-40 percent of the void volume, but did not adsorb (2). The experiments in sandy aquifer material support prior observations that virus particles can persist and travel several meters in sandy aquifers. Virus concentrations along the flow show evidence of dispersion but not retardation. Dispersion in the field was similar to that observed in the laboratory.

The phage f2 was largely excluded from the porous matrix of the twow fractured-rock cores studied, coming through 1.2 and 2.0 times later than predicted based on fracture flow alone. Non-sorbing solutes were retarded by over a factor of three relative to fracture flow due to matrix diffusion. Virus should thus travel 1.6-1.9 times faster than a conservative tracer. The time scale for a solute tracer to equilibrate with the porous matrix of 6.5-cm diameter by 25-cm long cores was on the order of days.

More recent column experiments carried out with silica beads as the model media illustrate that adhesion of the bacteriophage MS-2 (3) and PRD-1 (4) is slowly reversible at pH's 5-7. Chemical perturbations such as raising pH and introducing a surface-active chemical species enhance detachment. Despite the slow reversibility, isotherms have been developed for virus "adsorption" onto various natural and model surfaces. For example, recent experimental investigations illustrate greater MS-2 adsorption to a hydrophobic-bonded that unbonded silica surface (5).

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FLUID MECHANICAL CONSIDERATIONS ON COLLOIDAL TRANSPORT IN POROUS MEDIA

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Transport of colloidal particles (i.e., particles small enough to be kept in suspension indefinitely by Brownian motion) and suspended particles (i.e., particles small enough to be suspended over a limited time span but long enough to be transported over considerable distances) through porous media is conventionally explained by filter theory (1). However, this theory was developed to optimize the design of filters (i.e., porous media retaining such particles while allowing the fluid to pass through). A "conflict of interest" is apparent between the needs that motivated the development of filtration theory and questions related to understanding the extent to which colloidal particles can be transported through porous media.

There are reports of colloidal particles having been transported over distances between 10 and 1000 m within about 4 weeks (the life span of E. coli outside a warm-bloodied animal). The ratio of transport distance to particle size is between 107 to 109. Scaling this ratio up to the size of man results in transport distances that range from one earth circumference to the distance from here to the moon while the equivalent average travel velocity would be between 18 and 1800 miles/h. Intuitively, the existence of efficient transport seems to be a necessary condition to facilitate such rapid transport. Filter theory seems to be inadequate to deal with this phenomenon when the theory of water flow through porous media is based on the assumptions of continuity and average behavior within the medium. For further discussions see, for instance, McDowell el al. (2).

A kinematic wave approach to the transport of E. coli was introduced to address these issues. (The kinematic wave theory describes flow as a boundary-layer phenomenon and not as flow in a potential field. Therefore, it ignores any feed back between changes in soil moisture and related changes in soil moisture potential, it ignores any continuity requirements with respect to the entire porous medium, and gravity is the only force which drives flow.) The model parameters were derived from the experiments by Smith et al. (3) who percolated bacterial suspensions through undisturbed and reconstituted soil cores of about 0.2 m in diameter and 0.3 m long. Threshold values for parameters treating flow along preferred paths were defined. When applying these

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threshold to field conditions it was concluded that natural precipitation is either of too low an intensity or too short a duration to support colloidal transport over significant distances in unsaturated soils (say longer than 5 m). However, when doubling either the intensity or the duration of high intensity rain fall transport over distances of more than 20 m were predicted, using the macropore flow parameters reported so far. An increase of flow intensity may occur, for example, at the bottom of a hillslope or any other configuration that concentrates flow. For details see Germann et al. (4).

The fluid mechanical conditions for the entrainment of colloids from the surface of a solid into and by the liquid is not completely understood at the present. Even the theory of turbulent flow requires a non-slip condition, which includes the existence of a non-moving water film at the liquid/solid interface of about 0.01 mm thickness. This film is about 10 to 100 times thicker than the colloids being entrained from such a solid surface into the mainstream of the liquid. However, from studies of blood flow through the veins it is known that non-slip conditions may exist under some circumstances but not under others. Theoretical and experimental studies concerning flow at the solid/liquid interface at the scale of a single nanometer are under way.

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COLLOIDALLY-INDUCED FINES MIGRATION

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The area of "Colloidally-Induced Fines Migration" is of great importance, and finds applications in the petroleum industry, filtration of suspensions, migration of toxic wastes from dump sites and failure of earthen embankments. For the past decade, out research group at The University of Michigan has been actively involved in this area. Our interests in this specific area was motivated from the work in "Water Sensitivity of Sandstones", a problem of great concern to the oil industry. A detail knowledge in other disciplines was required to gain a fundamental understanding of the phenomenon. As a result of it's interdisciplinary nature, the expertise gained from our project is also useful in solving problems in other areas.

Experimental results show that porous sandstone cores initially saturated in brine show a drastic reduction in permeability when exposed to fresh water. Similar reductions in hydraulic conductivity are observed when the invading fluid is a low salinity brine. Scanning electron microscopy revealed that the reduction in permeability (referred to as "formation damage") was due to the blockage of fluids paths by sub-micron size particles (referred as "fines"). The detachment of these particles was triggered by changes in the colloidal conditions of the permeating fluid. The released fines migrate with the flowing fluid until they are trapped at pore constrictions, eventually leading to a decrease in permeability.

Some significant findings and results of our work are briefly described below.

1. There exists a critical salt concentration (CSC) above which the particle release is inhibited, and thus, the reduction in permeability is minimized. A mixture of cations (Na/Ca) and their effect on CSC has also been studied.
2. Flow reversal experiments showed that the reduction in permeability was a result of the migration of fines and not due to clay swelling as hypothesized by earlier researchers.
3. It was observed that the reduction in permeability can be controlled by a gradual decrease in salinity of the injected fluid. This led to the finding of a critical rate of salinity decrease (CRSD) beyond which no damage occurs.
4. A mathematical model was formulated, which incorporates the DLVO theory of electrical double layers. The model predicts observed experimental data accurately.

5. It was shown that the pH of the permeating fluid has an significant effect on the extent of damage. For Berea sandstone, the damage can be avoided if pH of the injection fluid is maintained below 2.6
6. Recent work has shown the correlative effects of pH and salinity. A model based on the principles of cation adsorption and ion-exchange show that salinity changes automatically induce changes in pH of the permeating fluid. This model, based on the fluid rock interactions, shows predictions similar to those observed experimentally.

COAGULATION OF COLLOIDAL IRON OXIDE PARTICLES IN WATER: SURFACE CHEMISTRY, ELECTROKINETICS AND DYNAMIC STABILITY

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Particles in the colloidal size range, i.e., smaller than 10^{-6} meter, are of interest in environmental science and many other fields of science and engineering. Since aqueous oxide particles have high specific surface area they adsorb ions and molecules from water, and may remain stable in the aqueous phase with respect to coagulation. Submicron particles collide as a result of their thermal energy, and the effective collision rate is slowed by electric repulsion forces. A key to understanding particle stability and coagulation is the role of simple chemical changes in the water altering the electrostatic repulsion forces between particles.

Experiments using hematite particles (d-Fe_2O_3, 70 nm in diameter) reveal important features of coagulation dynamics. Three experimental techniques were employed: (1) Light scattering measurements to yield quantitative information on the rate of the initial coagulation process; (2) electrokinetic measurements to provide information about the sign and magnitude of the electrical charge on the aqueous oxide particles; and (3) acid-base titration and equilibrium adsorption to obtain the intrinsic equilibrium constants for surface species.

The acid-base titration data indicate that the pHzpc of the synthesized hematite colloid is 8.5. This is also supported by the electrophoretic mobility measurements. In the presence of nonspecifically adsorbed ions (such as Na^+ and Ca^{2+}, etc.), the coagulation of a hematite colloid is achieved mainly by the compression of diffuse layer and Schulze-Hardy Rule is exhibited for nonspecific electrolytes. Specifically-adsorbed counter ions (such as phosphate) are able to reduce the surface charge of aqueous oxide particles; for these ions, the critical coagulation concentrations are dependent of the value of the pH and are much less than those predicted by DLVO theory. In inorganic media, we found that the order of the effectiveness in causing hematite particles to coagulate is:

$$\text{phosphate} > \text{sulfate} > \text{chloride at pH} < pH_{zpc}$$

and

$$\text{magnesium} > \text{calcium} > \text{sodium} \sim \text{potassium at pH} > pH_{zpc}$$

The adsorption study revealed that phthalate ions specifically adsorb on hematite particles. The process is most likely due to bonding of carboxyl groups to the surface. The hematite coagulation rates in the presence of poly-aspartic acid (PAA) demonstrate that the polyelectrolyte is very effective in causing the colloid to coagulate. However, when the PAA concentration is increased beyond the critical coagulation concentration, the particles are stabilized; this is attributed to the reversal of surface potential as a result of the adsorption of PAA. Similar features are observed in the initial coagulation rates when naturally occurring organics (fulvic and humic acid from Suwannee River) are used.

The adsorption of lauric acid on hematite was investigated and the results interpreted in terms of the energy contributed by the specific chemical, electrostatic and hycrophobic interactions. The initial coagulation rates of hematite particles and the electrophoretic mobilities with respect to fatty acid concentration both show systematic variations as a function of the numbers of carbons in the acid. Hydrophobic interaction may account for these observations since the specific chemical energy appears to be the same for all the fatty acids studied, and the electrostatic contribution is also similar at the same extent of adsorption.

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PARTITIONING BEHAVIOR OF GROUND WATER BACTERIA

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In an initial experiment, sorption of bacteria to soil was quantified by determining a bacterial soil:water partition coefficient, K_b, in test tubes. By using the K_b and a simple transport equation, bacterial migration through saturated soil columns was predicted. Predicted and measured migration rates were different. In an effort to explain these discrepancies, the influence of nutrients and suspended material on bacterial sorption to soil was investigated, and other methods of measuring K_b were tested.

Groundwater bacteria were labelled with radioactive isotopes, and added to four different glass vials containing soil and water. The soil consisted of suspended particles less than 630 or 60 um in diameter. The water was either filter-sterilized groundwater or lake water. At different time intervals, bacteria in the soil- and water-phase were separated by differential centrifugation, and radioactivity measured using liquid scintillation counting. In calculating the K_b, compensation for bacterial metabolism of the labelled compounds was made.

The time needed to reach a sorption equilibrium varied depending on the glass vials and water used. The bacterial soil:water partition coefficients also varied, but not always in the same pattern. The K_b was highest using a sorption cell with a continuous flow of water, and was lowest in the test tubes. Using this sorption cell, sorption of bacteria to soil was initially higher with groundwater compared to incubations using the filter-sterilized lake water, but in time the sorption leveled off to reach the same value as in lake water. The leveling off coincided with an increased sorption to the glass. The sorption isotherm with bacteria and suspended material showed that up to 73% of the bacteria were sorbed.

The results demonstrate that K_b's measured in test tubes can clearly underestimate bacterial sorption and overestimate bacterial migration rates. On the other hand, the suspended material leaching from a soil column could facilitate bacterial migration, since it was shown that up to 73% of the bacteria sorbed to this fraction. The sorption of bacteria to soil changes with time, and important factors governing the change include hydrodynamics, oxygen and nutrient levels.

DEGRADATION AND PARTITIONING OF NAPHTHALENE IN SOIL

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The fate of naphthalene (a polynuclear aromatic hydrocarbon) in water-saturated (200% moisture) and unsaturated (10% moisture) soils has been studied by headspace batch equilibration. Changes in concentration of naphthalene were monitored by headspace sampling, and solvent extraction of the reaction mixture. The trends for sorption of naphthalene are similar under both saturated and unsaturated conditions involving initial loss of naphthalene, a temporary steady state within 24-48 h, and then a gradual steady loss which sets in after about 3 d. The steady-state concentration is approximately 65% and 30% of initial value respectively for saturated and unsaturated soils. Also at steady state, less than 1% of recovered naphthalene is associated with gas phase in saturated and unsaturated soils; while >70% of naphthalene is associated with solid particles in saturated soil. This greater degree of association of naphthalene with solid particles could be due to dispersion of colloidal clay minerals under saturated conditions, exposing greater surface area for adsorption. The significance of this is enhanced transport of napthalene down the soil profile by colloidal clay particles in high soil water conditions. This trend may also be true for other polynuclear aromatic hydrocarbons.

TRANSPORT AND RETENTION OF MICROSPHERES AND DISSOLVED ORGANIC CARBON IN SAND COLUMNS

Laura E. Toran, Anthony V. Palumbo, and John McCarthy
Oak Ridge National Laboratory

We have studied the effects of fractures on microparticle transport in laboratory sand columns. This research has implications for predicting the role of fractures in contaminant transport, for understanding the influence of microbial transport in bioremediation of contaminated aquifers, and for studying the transport of colloids in porous media.

We designed laboratory sand columns that can include capillary tubes 1 mm in diameter to simulate fractures. In separate experiments, we injected fluorescent microspheres 1 um in diameter, dissolved organic carbon (DOC) from a forested stream (approximately 30 mg carbon L^{-1}), and a conservative salt tracer into columns with and without capillary tubes. The effluent concentration of these tracers was measured as a function of time to obtain a breakthrough curve.

The presence of the capillary tubes significantly decreased retention of the colloids in the column. Retention of the DOC was 1.5 times lower with tubes, and more than 10 times lower for the microspheres, compared to columns without the capillary tubes. Colloids tended to travel faster than the conservative tracer, with "retardation" factors of 0.9 to 1.0. The faster travel time is probably caused by filtration of the microspheres in the matrix that excluded travel at the slower velocities within the matrix. However, neither dispersion nor porosity were significantly higher in the "fractured" system than in the "unfractured" system.

Multiple breakthrough curves for the microspheres were produced when transport through the matrix was almost completely inhibited by chemical sorption. We hypothesize these breakthrough curves reflect different lengths of travel through the matrix, with most of the flow path going through the tubes.

Our research using artificial fractures in laboratory sand columns suggests that fractures can significantly increase transport of colloids and that colloids may provide additional information about pathways of transport through fractures, information that is not available from soluble tracers alone.

SESSION III

DISCUSSION OF COLLOIDAL TRANSPORT AND DEPOSITION

Objective of the Session: The oral presentations and discussion following those presentations addressed many of the important questions concerning colloid transport and deposition. These discussion sessions were intended to provide a forum to summarize the group consensus on important issues and try to resolve conflicting views.

Discussion Topic A

Natural Conditions Favoring Colloid Transport or Deposition
Moderated by John M. Zachara [Batelle Pacific Northwest Laboratory] and
James R. Hunt [University of California, Berkley]

Discussion Topic B

Strategies to Manipulate the Behavior of Groundwater Colloids for Hazardous Waste Management
Moderated by Laura E. Toran [Oak Ridge National Laboratory]

SESSION III
DISCUSSION TOPIC A

NATURAL CONDITIONS FAVORING COLLOID TRANSPORT OR DEPOSITION

Moderated by
John M. Zachara [Batelle Pacific Northwest Laboratory]
and
James R. Hunt [University of California, Berkley]

Objective of the Session: *To identify natural environmental conditions of aqueous chemistry, mineralogy, hydrology, etc., that favor either the transport or the deposition of colloidal particles. The intent of this discussion is to focus research efforts on those natural subsurface environments with the greatest probability for occurrence of mobile colloids.*

A group discussion was held to identify the natural subsurface conditions of aqueous chemistry, mineralogy, and hydrology that favor the genesis, transport, and deposition of colloids in groundwater environments. This discussion centered around ideas summarized in Fig. 1. The technical findings of this discussion are summarized below.

A first but essential step in the genesis of a mobile colloidal fraction in groundwater is their 1) translocation to the groundwater zone from soil, 2) release from the porous media, or 3) direct formation in the aqueous phase from homogeneous precipitation or micro-polymer aggregation (Fig. 1). If these colloids are stabilized in the suspended state through surface chemical interactions (e.g., resist sedimentation or interparticle aggregation or flocculation) the potential exists for their downgradient migration with fluid movement in the aquifer. The ultimate mobility of colloidal particles will be controlled by factors such as the extent of downgradient aggregation/straining filtration or physicochemical collection.

Participants indicated that translocated colloids were most prevalent in shallow groundwaters near the recharge zone. The infiltration of low ionic strength precipitation and meteoric waters into certain soils with low salt content may destabilize aggregates of clay, oxides, or organic material generating potentially mobile colloids. Highly structured soils with cracks and macropores facilitate migration of soil derived colloidal material to depth because the prospects for particle filtration or collection are diminished. Organic colloidal material of translocated origin has often been found in groundwaters recharged by bog water.

It was generally believed that geochemical gradients of either natural or anthropogenic origin, or the mixing of groundwaters of unlike composition were of greatest importance in the genesis of mobile colloids. Geochemical gradients exist when groundwater composition and/or pH change in the downgradient direction as a result of geochemical/microbiological processes or through contaminant infiltration. Changes in variables such as pH, oxidation-reduction potential, CO_2 or HS partial pressure can induce the supersaturation of mineral phases in groundwater leading to homogeneous precipitation of inorganic colloidal material, or alternatively, the dissolution of mineral cements binding aggregated material together. Water compositional changes such as a reduction in ionic strength or change in the ion balance from that dominated by Ca to that dominated by Na can disperse stable aggregates of colloidal material bound to the mineral matrix thereby releasing colloidal material to the groundwater phase. The genesis of mobile colloids may occur in contaminant plumes because of water chemistry differences between native groundwaters, and because higher DOC and nutrient concentrations within the plume promote the disattachment of microorganisms.

Agreement was considerable that colloidal material released to groundwater must be stabilized from the surface chemical perspective to be potentially mobile within the aquifer. Discussion focused around the conditions and factors governing colloid stability (Table 1). Particular emphasis was placed on the Fe and Si oxides, layer lattice silicates, and organic material, constituents that appear to dominate the mobile colloid load in groundwater. Surface complexation models were identified as essential tools that have been used to quantitatively relate the effects of electrolyte concentration, pH, and surface complexes with inorganic ions to diffuse layer potential and surface charge. The noted occurrences of colloids in groundwater was concluded to be qualitatively in accord with DLVO theory and the empirical Schulze-Hardy rule. Jim Morgan noted that he was currently preparing diagrams to estimate the stability of colloidal material in natural waters that would be useful in identifying the conditions of groundwater chemistry that would promote colloid stability in the aqueous phase.

Once stabilized in the groundwater phase, colloids may still not be mobile if they are removed via coagulation/aggregation and straining filtration or by physicochemical collection. Participants noted that particle filtration, coagulation, and collection phenomena were not well understood in simple model systems. Physicochemical collection occurs when the colloidal material binds to the aquifer matrix via a surface chemical interaction. While collection is obviously favored when the surface and colloid carry opposite charge, it can and does occur to a more limited degree when both colloid and surface carry the same net charge. Predictions of physicochemical collection by "state of science" models often error by significant margins, especially when particles and surfaces carry like charge, suggesting that the process is not well understood. Thus significant research is needed to identify the importance of these phenomena in groundwater and to establish the chemical, physical, and hydrologic controlling their manifestation and magnitude in aquifers. Further, models do not exist to estimate the rate of coagulation of colloids as a function of pH, ionic strength, particle size, and concentration if geochemical conditions change to destabilize the colloid load. In general however, it was noted that mobile groundwater colloids often carry net negative charge, as do most aquifer solids. Thus, these mobile particles are those that are least likely to be removed from the aqueous phase through particle collection.

Limited field evidence suggests that colloidal material may be transported over significant distances if the water bearing zone is highly transmissive or contains significant areas of macroporosity. Hydrologists argued that many subsurface zones are highly transmissive where micron sized colloids would be readily mobile if they were not removed by particle collection. Preferential flowpaths where particles may be shunted past large volumes of porous media through cracks, fissures, or zones of significant secondary porosity were cited by many as the major pathway through which colloids migrate in the subsurface. While preferential flow paths may be most important in structured soils, fractured bedrock, and karst terrain, increasing evidence using tracer experiments with microspheres suggests that macroporosity of unknown origin may control particle transport in unconsolidated aquifer materials of recent sedimentary origin. Final discussions focused on the need for studies and techniques to characterize the extent and flow properties of preferential flow paths in sedimentary porous media that characterize most near surface aquifer systems.

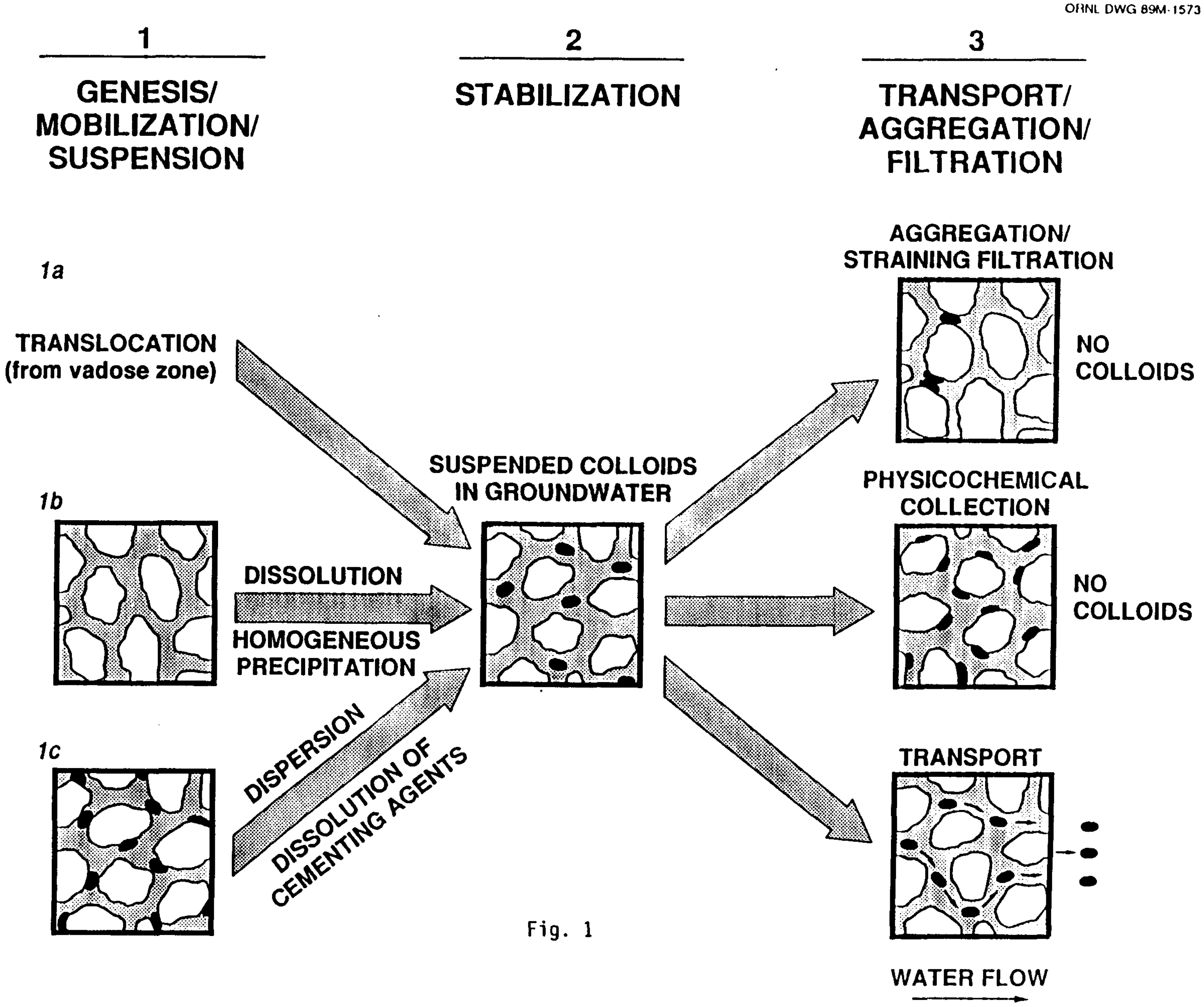
ORNL DWG 89M-1573
1
GENESIS/ MOBILIZATION/ SUSPENSION
2
STABILIZATION
3
TRANSPORT/ AGGREGATION/ FILTRATION
1a
TRANSLOCATION (from vadose zone)
1b
DISSOLUTION
HOMOGENEOUS PRECIPITATION
1c
DISPERSION
DISSOLUTION OF CEMENTING AGENTS
SUSPENDED COLLOIDS IN GROUNDWATER
AGGREGATION/ STRAINING FILTRATION
NO COLLOIDS
PHYSICOCHEMICAL COLLECTION
NO COLLOIDS
TRANSPORT
WATER FLOW

Fig. 1

TABLE 1. Factors influencing the stability of colloid suspensions

Factor	Effect	Promotes coagulation	Promotes stability
Electrolyte concentration	Extent of DDL[a] solvation Force	When increased	When decreased
pH	Changes σ_H[b]	pH = pzc[c]	pH ≠ pzc
Surface complexes with ions	Changes σp[d]	$\sigma p = 0$	$\sigma p \neq 0$
Surface complexes with polyelectrolytes	Changes σP and/ or particle association	With polymer bridging	By electrostatic repulsion
Organic cosolvents	Extent of DDL Solvation Force	When increased (IC)[e] When decreased (OC)[f]	When decreased (IC) When increased (OC)

Source Reference 35

[a] DDL = diffuse double layer.

[b] σ_H = net proton charge.

[c] pzc = pH of the point of zero net surface charge.

[d] σp = net total particle charge.

[e] IC = inorganic colloids.

[f] OC = organic colloids.

SESSION III

DISCUSSION TOPIC B

STRATEGIES TO MANIPULATE THE BEHAVIOR OF GROUNDWATER COLLOIDS FOR HAZARDOUS WASTE MANAGEMENT

Moderated by Laura E. Toran [Oak Ridge National Laboratory]

Objective of the Session: *To explore strategies to manipulate colloid mobility in subsurface systems, particularly at waste sites, in order to prevent, mitigate, or remediate groundwater contamination.*

A variety of remediation techniques have been used at different waste sites. These techniques fall into two broad categories: treatment of the contaminants and containment. Treatment technologies may involve biological, chemical, or physical processes while containment has so far emphasized physical barriers.

If treatment is the goal, then enhancing colloid mobility may help remove both groundwater contaminants and contaminants sorbed to the matrix. The colloid-bound contaminants could be pumped to the surface for removal or treatment. If containment is the goal, it would be important to understand whether colloids provide a transport vector and whether immobilization of colloids could be used to enhance containment. The possibility of using colloids to reduce permeability as a containment strategy has been studied in the laboratory, but not on a field scale where large scale structures (e.g., fractures) may inhibit pore clogging.

In general, containment strategies involving colloids are more problematic than treatment strategies because of the need to control and predict long term behavior, which is fraught with uncertainties. In a treatment system, there is immediate feedback on the success or failure of the mobilization process when groundwater is pumped to the surface and tested.

The challenges for research on the role of colloids in remediation strategies are similar to those affecting other areas of colloid research, including difficulties in obtaining representative samples, understanding contaminant interactions, and characterizing preferred flow paths. In addition, remediation implies dealing with regulatory/political factors such as demands for economical, low risk strategies.

The consensus of the group was that these challenges need to be met by taking a mechanistic approach to understand colloid- bound contaminant transport and immobilization. There needs to be increased emphasis on exploring empirical observations in the field as well as performing field scale experiments. The consensus was that, even with all the uncertainities surrounding our understanding of colloid behavior, there is sufficient experience and expertise to begin pilot studies to test the more straightforward strategies for manipulating groundwater colloids. It was felt that some very applied research addressing site-specific problems could also contribute substantially to understanding colloid behavior, especially if undertaken in collaboration with basic research on the hydrogeochemistry of colloidal particles in groundwater.

SESSION IV

IDENTIFICATION AND PRIORITIZATION OF RESEARCH NEEDS

Moderated by John F. McCarthy [Oak Ridge National Laboratory]

Objective of the Session: To achieve a group consensus on research priorities for understanding the role of colloidal particles in the transport of contaminants in the subsurface environment. The draft of the DOE Colloid Subprogram Research Plan was distributed to participants prior to the meeting and served as a focus for discussion.

To facilitate discussion, the "strawman" which was modified as a result of the group discussion, list of research priorities described in the draft of the DOE Colloid Subprogram Research Plan was presented for discussion. The priorities were presented as a series of task/milestones based on an assumption that the research program would last 5 years and be constrained to a total budget of $5 million. That "strawman" is summarized below:

PHASE I: YEARS 1-2 ($1 million) -- Two major goals will be pursued during the initial phase of this research:

1. *Conduct an intensely monitored field experiment to observe the migration of organic colloids injected into the saturated zone of a shallow unconsolidated sand aquifer.*
2. *Develop/test/publish a sampling protocol suitable for collecting particulate material in the mobile phase of soil water and groundwater. Validation of protocols will require development of a network of research sites.*

PHASE II: YEARS 2-4 ($1.5 million) -- The goal of the second phase of research is to determine what, if anything, is unique about colloids recovered from subsurface environments:

1. *Characterize the physicochemical properties of colloidal particles, with special emphasis on the surfaces of colloidal particles. Use of advanced instrumentation such as tunneling microscopes and ESCA is encouraged.*
2. *Determine the suitability of available expressions to predict sorption of organic, metal, and radionuclide contaminants to organic and inorganic particles. Develop new expressions if necessary.*

<u>PHASE III:</u> YEARS 3-5 ($2.5 million) -- The goal of this phase of research is to describe and test predictive expressions of colloid transport through porous media:

1. *Determine the suitability of available expressions for colloid stabilization and deposition as a function of colloid and collector surface properties. Use natural subsurface material and test chemical conditions typical of vadose and saturated zone environments.*
2. *Develop expressions to describe the hydrologic controls of colloid transport. Develop methods to characterize critical hydrogeological variables in situ.*
3. *Test predictions of colloid transport in one- and multidimensional laboratory columns and in an intermediate-scale facility. Emphasize development and testing of strategies for manipulating colloid mobility.*
4. *Examine effects of real-world heterogeneity, using stochastic descriptions if appropriate, at an instrumented field site.*

The discussions critiqued this initial "strawman" and lead to an improved set of priorities and milestones. That discussion is summarized here, as are the priorities and milestones that resulted from the discussions. The consensus of the group was that sampling and characterization of colloidal particles in groundwater should be the highest priority. Information on sampling methods and on quantification and characterization of groundwater colloids needs to be obtained from a network of field sites that can be studied on a comparative basis by collaborating researchers. These sites should attempt to bound a range of conditions in which colloids may occur. It was clear that no easy consensus could be reached on the location and specific characteristics of those field sites, and it was suggested that a workshop may be useful to establish the hydrgeochemical conditions to be bounded and to identify appropriate field sites. For the present, existing DOE field sites in North Carolina, South Carolina, New Jersey and Delaware are appropriate field sites for comparative and collaborative studies.

While the field injection experiments were judged to be a valuable contribution, it was considered to be more appropriate as a second phase of a colloid research plan. This discussion lead to a general debate on the proper mix of laboratory and field research. The consensus was that both are necessary and proper, and ideally should involve an iteration between laboratory studies to describe fundamental phenomena, and field studies to determine the occurrence and behavior of colloids in natural systems.

There was considerable debate about how to approach the hydrologic expression of colloid transport. Hydrologic research includes mathematical and physical expression of transport. While one school of thought felt that these problems had been solved, at least for many engineering applications, others argued that the existing solutions have not been solved in a way that can be applied to the "real world" of heterogeneous natural environments.

Modeling of colloid transport and its effect on contaminant mobility needs to be integrated within experimental designs from early stages of both laboratory and field research. It was felt that model development needed to take into account the experimental realities that limit the data available for parameterizing the models, and experimentalists and field scientists need to be sensitive to types of information required for developing models. In general, a coherent research program needs to explicitly integrate field observations, laboratory experimentation, and model development from the earliest stages of program development. It was also noted that aggregation was a topic that was not clearly addressed, and was a level of complexity not dealt with in current models.

Based on this discussion and on written suggestions by participants, the priorities for the DOE Colloid Research Plan were modified:

> Initial research in the DOE Colloid Subprogram needs to focus on two questions: <u>Do</u> colloids exist and <u>why</u> do they exist? Answers to these questions will also provide information relevant to waste management and remediation. Laboratory studies have an important and critical role in this research plan, but priority will be given to research in which experimental questions are driven by, and tested in, field systems. While understanding of mechanisms of contaminant-colloid interactions is obviously important, existing predictive capabilities or empirical, site-specific measurements can provide a general indication of the significance of mobile colloids to contaminant transport; this component of research will, therefore, receive secondary priority. Based on this philosophy, priorities are assigned in the following order:

1. <u>Colloid sampling and characterization</u> -- This problem is fundamental to all other questions. Unless groundwater colloids can be sampled and described in terms of their physical and chemical properties, all other research questions are moot.

2. Colloid generation and deposition -- What basic chemical, hydrological, and mineralogical properties of a subsurface system are associated with formation of stable colloidal suspensions in groundwater? Studies of model subsurface environments bounding ranges of system properties can elucidate conditions favoring the genesis of colloids or their deposition on the aquifer media.
3. Colloid mobility -- If stable colloids exist, do they move? At experimental field sites, is colloid movement dependent primarily on chemical factors (e.g., electrostatic interactions) or physical and hydrologic features (e.g., presence of fractures or other preferential flow paths)?
4. Waste management/remediation demonstration -- Based on understanding of system properties affecting colloid formation, deposition and transport, a demonstration of the application of this understanding to waste problems at DOE sites will receive a high priority.

Given the priorities established above, specific research tasks are outlined in three phases in roughly chronological order of implementation. It is recognized that Phases can and will overlap to varying degrees at different field sites, depending on the tractability of problems encountered at each environment.

PHASE I: YEARS 1-3 ($1.7 million) -- Three major tasks will be pursued during this initial phase of research:

1. Sampling and Characterization Protocols -- Develop, test, and compare methods for sampling colloidal particles and test and compare methods for characterizing their physical and chemical properties, including methods for concentrating colloids from dilute groundwater suspensions. Investigators within the program need to decide on acceptable protocols for intercomparison of results from different field sites.
2. Network of Reference Subsurface Environments -- Establish a network of reference or model subsurface environments that bound a range of conditions where colloids may occur. A workshop may be useful for establishing those bounds and identifying field sites.
3. Characterizing Colloids from Field Sites -- Systematically investigate the abundance and properties of colloidal particles at the range of field sites established in Task 2, using methods agreed on in Task 1. At each site, research should investigate why the colloids are or are not present, and what chemical, hydrological and mineralogical factors control colloid formation

and deposition. Laboratory research will be conducted to test hypotheses derived from field observations.

PHASE II: YEARS 1-4 ($2.3 million) -- This phase of research consists of one major task, Field Experimentation. Whereas Phase I consisted of observation of colloids under natural conditions, Phase II uses intermediate scale facilities and field sites to experimentally manipulate systems to: (a) demonstrate that colloids move -- how fast and how far; (b) test effects of chemical and hydrologic factors in colloid formation and transport at a field scale; and (c) test methods to manipulate colloid mobilization and deposition for waste remediation. Possible field sites include some of the reference sites in Phase I, DOE Subsurface Environmental Research Facilities, and possibly DOE waste sites. As with other phases of research, laboratory experiments will be conducted to test hypotheses and confirm understanding.

PHASE III: YEARS 4-5 ($1 million) -- The goal of this phase is to consolidate and refine understanding gained from previous phases in the formulation of predictive models. The objective will be a demonstration of (1) capabilities to predict colloid-facilitated transport at a DOE waste site, and (2) chemical remediation at a waste site based on manipulation of subsurface colloidal particles. The actual demonstration of predictive capabilities and site remediation may be considerably more costly than is reflected in the proposed budget; it is assumed that most of the cost of the site work will be born by the DOE Operations Office at the site, based on preliminary successes achieved in Phase II.

The goals of this phase of research are ambitious, although the level of funding reflects the degree of expected difficulty. Progress to these goals will depend, to some extent, on advances achieved in other components of the DOE Subsurface Science Program. For example, problems in characterizing and modeling heterogeneous systems are not unique to colloid research but constrain progress in many aspects of contaminant transport research.

Further information on the scope, objectives, and priorities of the DOE Colloid Subprogram of the Subsurface Science Program can be found in: McCarthy, J. F. Role of Colloidal Particles in the Subsurface Transport of Contaminants: Five Year Subprogram Plan for the Department of

Energy Subsurface Science Program; DOE/ER-0384, U. S. Department of Energy: Washington, D.C., 1989.

APPENDIX A

AGENDA OF THE MEETING

INTERNATIONAL SERIES OF INTERACTIVE SEMINARS

MOBILITY OF COLLOIDAL PARTICLES IN THE SUBSURFACE: CHEMISTRY AND HYDROLOGY OF COLLOID-AQUIFER INTERACTIONS

OCTOBER 4-6, 1988
MANTEO, NORTH CAROLINA

Organized by:

John McCarthy
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in cooperation with:

Frank J. Wobber
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OBJECTIVE OF THE MEETING: *To examine the chemical and hydrologic factors controlling the transport and deposition of organic and inorganic colloidal particles in subsurface environments.*

Monday Evening, October 3, 1988

Reception and Mixer (Elizabethan Inn)

Tuesday, October 4, 1988

8:30 - Purpose and Objective of Meeting

J. F. McCarthy [Oak Ridge National Laboratory]

8:50 - Scope of DOE Subsurface Transport Program

F. J. Wobber [Department of Energy]

SESSION I. SAMPLING AND CHARACTERIZATION OF COLLOIDAL PARTICLES IN GROUNDWATER

Moderated by Philip M. Gschwend [Massachusetts Institute of Technology]

Objective: To discuss difficulties in sampling and characterizing colloidal particles in groundwater and critically review innovative approaches.

9:15 - Introduction to Sampling Problems
P. Gschwend [MIT]
9:30 - The Characterization and Properties of Colloidal Particulates in Aqueous Media
J. D. F. Ramsey [Harwell Laboratory, UKAEA]
10:15 - BREAK
10:30 - Characterization of Colloids in Groundwater Using Laser-Induced Photoacoustic Spectroscopy
J. I. Kim [Technischen Universitat Munchen)
11:15 - Sampling and Characterization of Colloids in the Canadian Nuclear Fuel Management Program
P. Vilks [Whiteshell Nuclear Research Establishment]
12:00 - LUNCH

Tuesday, October 4, 1988

SESSION I (continued)

1:00 - Sampling and Analysis of Colloids in Groundwater at the Nevada Test Site
L. Kingston, R. Jacobson, and M. Whitbeck [Desert Research Institute]
1:30 - An Approach to Studying Radionuclide Transport by Colloids in Natural Rock/Water Systems
G. Longworth and M. Ivanovitch [Harwell Laboratory, UKAEA)
2:00 - Distribution and Characterization of Bacteria in Groundwater
D. L. Balkwill [Florida State University]
2:45 - BREAK

SESSION II. CHEMICAL AND HYDROLOGIC FACTORS CONTROLLING COLLOID TRANSPORT

Moderated by J. F. McCarthy [ORNL]

Objective: *To critically review observations of colloid movement in laboratory and field systems, with an emphasis on the chemical and hydrological factors controlling transport.*

3:00 - Movement of Colloidal Particles in Saturated Media at The Chalk River Nuclear Research Laboratory

D. R. Champ [Chalk River Nuclear Research Laboratory]

3:45 - Colloid-Facilitated Transport in Groundwater: Laboratory and Field Observations

B. B. Looney [Savannah River Ecology Laboratory], M. E. Newman, and A. W. Elzerman [Clemson University]

4:30 - POSTER SESSION AND SOCIAL

Wednesday, October 5, 1988

SESSION II (continued)

8:45 - Formation and Mobilization of Colloidal Particles in Contaminant Plumes

P. M. Gschwend [MIT]

9:30 - Chemical and Hydrologic Factors Controlling the Transport of Organic Colloids

J. F. McCarthy, P. M. Jardine, and N. Weber [ORNL]

10:15 - BREAK

10:30 - Transport of Organic Macromolecules in Porous Media

C. G. Enfield [U.S. Environmental Protection Agency]

11:15 - Mobility of Microorganisms in Porous Media

R. W. Harvey [U.S. Geological Survey, Menlo Park]

12:00 - LUNCH

1:00 - Observations in Biocolloid Transport in Saturated Systems

C. Gerba and R. Bales [University of Arizona]

1:45 - Fluid Mechanical Considerations on Colloidal Transport in Porous Media

P. F. Germann [Rutgers University]

2:30 - BREAK

2:45 - Colloidally Induced Fines Migration in Porous Media
H. S. Fogler [University of Michigan]

SESSION III: DISCUSSION OF COLLOIDAL TRANSPORT AND DEPOSITION

Objective: The oral presentations and discussion following those presentations will address many of the important questions concerning colloid transport and deposition. These discussion sessions are intended to provide a forum to summarize the group consensus on important issues and try to resolve conflicting views.

III.A. NATURAL CONDITIONS FAVORING COLLOID TRANSPORT OR DEPOSITION

Moderated by John M. Zachara [Batelle Pacific Northwest Laboratory] and J. R. Hunt [University of California, Berkley]

Objective: To identify natural environmental conditions of aqueous chemistry, mineralogy, hydrology, etc., that favor either the transport or the deposition of colloidal particles. The intent of this discussion is to focus research efforts on those natural subsurface environments with the greatest probability for occurrence of mobile colloids.

3:30 - Review of the Problem

3:45 - Group Discussion

5:00 - SOCIAL HOUR

Thursday, October 6, 1988

III.B. STRATEGIES TO MANIPULATE COLLOID TRANSPORT OR DEPOSITION

Moderated by L. E. Toran [Oak Ridge National Laboratory]

Objective: To explore strategies to manipulate subsurface systems, particularly at waste sites, and promote deposition of colloids (not only to prevent colloid-assisted transport, but perhaps also reduce aquifer permeability and further retard contaminant transport).

8:30 - Review of the Problem
8:45 - Group Discussion
9:45 - BREAK

SESSION IV: IDENTIFICATION AND PRIORITIZATION OF RESEARCH NEEDS

Moderated by J. F. McCarthy [ORNL]

Objective: *To achieve a group consensus on research priorities for understanding the role of colloidal particles in the transport of contaminants in the subsurface environment. The draft of the DOE Colloid Subprogram Document will be distributed to participants prior to the meeting and will serve as a focus for discussion.*

10:00 - Overview of DOE Colloid Subprogram
10:20 - Group Discussion
12:00 - Adjournment

APPENDIX B

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