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NATURAL GELS IN THE YUCCA MOUNTAIN

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Colloid-Facilitated Radionuclide Transport at Yucca Mountain

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Abstract

The objective of this report is to describe the colloid investigations within the Yucca Mountain Site Characterization Project to evaluate whether colloids will significantly increase radionuclide release from a potential high-level nuclear waste repository at Yucca Mountain to the accessible environment. The evidence of the existence of colloids from sampling studies and observation of colloid transport at the field scale are reviewed. The relevance of colloid transport laboratory and field experiments to the conditions at Yucca Mountain are discussed. Research needs are identified in the areas of: colloid sampling, colloid generation, colloid stability, colloidal sorption/desorption of radionuclides, and colloid migration. The colloid transport calculations that will allow evaluation of the data to assess the importance of colloid-facilitated radionuclide transport at Yucca Mountain are presented.

Introduction

The role of colloids in the transport of contaminants through the subsurface was reviewed by McCarthy and Zachara (1989). These authors concluded that the existing data suggest that colloidal species can enhance contaminant transport in the subsurface in the vadose and the saturated zones. McCarthy and Zachara also point out that the existing information is inadequate to assess the importance of colloid-facilitated transport or to develop a predictive capability that includes colloids for the prediction of contaminant migration. The work of McCarthy and Zachara identifies several research needs: development of sampling techniques and predictive capabilities to determine the occurrence and properties of subsurface colloids, experiments and predictive transport models to assess the mobility of subsurface colloids, and contaminant sorption data onto colloids to evaluate the implications of colloids for contaminant transport in the subsurface.

Ramsay (1988) reviewed the role of colloids in the release of radionuclides from a nuclear waste repository. Ramsay defines colloids as particles in the size range from 1 nm to 1 μ m with large surface areas (on the order of 10^3 m²/g for the smallest particles). This author points out that the role of colloids in migration involves many processes such as: enhancement of the source term by the leaching of the radionuclides in colloidal form from the waste form, degradation of the waste form (by bacterial action) producing fine particulates, and sorption of radionuclides onto colloids present in the groundwater. Ramsay points out that although it is clear that colloids exist, their significance in affecting radionuclide migration is not clear. Ramsay's work describes three general cases for colloid-facilitated radionuclide migration: uncharged colloid particles

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(that are considerably smaller than the pore or fracture size of the medium) which migrate without retardation, charged colloids that have the same sign as the surface charge of the medium and that are repelled by the medium walls resulting in a net increase in colloid flow velocity, and the case of colloids and the medium surfaces having opposite charges which could result in a slowing down of the colloid particles by interaction with the medium.

There are two main colloid categories in the subsurface in a nuclear waste repository: groundwater colloids and anthropogenic colloids. Groundwater colloids (Kim, 1991) are naturally occurring in aquatic systems and consist of inorganic and/or organic molecular constituents or microorganisms. Anthropogenic colloids are colloids produced by physical, chemical, or biological processes acting on human-introduced materials. These include radioactive waste-derived colloids and colloids derived from other materials and activities related to waste isolation.

Radioactive waste-derived colloids include:

- a) degradation colloids which are generated by disaggregation or spalling of actinide solid phases directly from the waste form.
- b) precipitation colloids which are generated from solutions that are supersaturated with respect to actinide solid phases. These may include real actinide colloids produced by the agglomeration of hydrolyzed actinide ions which are traditionally referred to as radiocolloids.
- c) pseudocolloids which are generated by the attachment of radionuclides (in soluble or colloidal form) to other colloids (such as groundwater colloids).

The objectives of this report are to describe colloid transport models that can be used to assess the importance of colloid-facilitated radionuclide migration, summarize the observations of the existence of colloids from sampling studies and the evidence of colloid transport at the field scale, list the potential sources of colloids at Yucca Mountain, review the colloid transport experiments relevant to a potential nuclear waste repository at Yucca Mountain, and summarize the research questions that need to be answered in order to predict the role of colloids in radionuclide release from a potential repository at Yucca Mountain.

Background on Geochemical Setting

Yucca Mountain is an accumulation of ash-flow tuff units; most units retained enough heat after deposition to develop densely welded, devitrified interiors in which the original glass particles consolidated and crystallized to a high-temperature assemblage of feldspars and silica minerals (Levy, 1992). Levy reports that the upper and lower margins of the units remain vitric; thinner, bedded tuffs between the main ash flows are

also vitric and nonwelded. In the middle and lower tuff units, most glassy tuffs have diagenetically altered to hydrous assemblages dominated by zeolites. Levy (1992) points out that the proposed high-level nuclear waste repository at Yucca Mountain would be located within the densely welded devitrified tuff of the Topopah Spring Member of the Paintbrush tuff. A vitrophyre underlies the location of the proposed repository. The saturated zone at Yucca Mountain is 300-700 m below land surface; 200 to 400 m below the base of the proposed repository.

The water chemistry at Yucca Mountain was reviewed by Meijer (1992). In the volcanic units, the groundwaters are dilute sodium bicarbonate waters. Sodium, calcium, potassium, and magnesium are the major cations; bicarbonate sulfate, chloride, nitrate and fluoride are the major anions in order of decreasing concentration. The only other major constituent is silica. The water from the Paleozoic aquifer has higher concentrations of virtually all constituents listed above. The concentration of the major cations and anions in unsaturated zone groundwaters appears to be intermediate between the saturated zone tuffaceous waters and waters from the carbonate aquifer. Most of the waters at Yucca Mountain are oxidizing; the pH of the waters range from 6.5 to 9.4.

Colloid Transport Calculations

Figure 1 illustrates the major processes that may occur during the migration of colloids in the subsurface: colloidal generation, sorption of radionuclides onto colloids in the groundwater, attachment /detachment of colloids, agglomeration of colloids in the groundwater, and exclusion of colloidal particles from pores due to size or surface charge considerations. The limited applicability of filtration theory to describe particle transport through porous media has been discussed by McDowell-Boyer et al. (1986) who concluded that data were needed on particle retention, aggregate formation, permeability reduction, and the potential for erosion by changes in flow or solution chemistry before colloid transport through a natural aquifer could be predicted. Smith and Degueudre (1993) pointed out the limited applicability of filtration theory to describe colloid transport through fractured media where colloid-wall interactions are important. Kessler and Hunt (1993) described the result of deposition and erosion of colloids in fractured media. They reported that colloids suspended in the water in fractures will deposit on fracture surfaces and partially or completely clog the fracture; the degree of clogging depends on whether deposited colloids can erode from the surfaces of the fractures. When the fracture remains only partially clogged the unclogged portion becomes an open channel. Kessler and Hunt predict that for repository conditions (involving very low flow rates ~ 1 m/y) erosion will not occur and the colloids will not travel very far because the fractures are expected to clog up completely with colloids.

The code CTCN (Colloid Transport Code - Nuclear) was developed within the Yucca Mountain Site Characterization Project for the study of colloid transport in porous and fractured media under unsaturated and saturated conditions (Jain, 1991). The CTCN

code was designed to solve the unsteady population balance equations along with mass, energy, and momentum equations in up to four axes. This code uses the Method of Lines with Modified Gear Method to solve the population balance equation; it is written in FORTRAN 77 and is capable of running on SUN, VAX, and CRAY systems. CTCN maintains a mass balance of the particles in the system and is capable of taking into account the colloid transport phenomena in Figure 1 in order to describe colloid migration through a natural medium. Most other colloid transport calculations (e.g., Smith and Degueldre, 1993) are performed with transport codes for soluble contaminant migration using parameters and boundary conditions that simulate colloid behavior.

Colloid-facilitated radionuclide transport was investigated in two dimensions for saturated and unsaturated fractures by Nuttall et al. using CTCN (1991). A steady-state parabolic flow velocity profile was assumed for these calculations and a step input of colloids was used as a boundary condition to introduce particles into the fracture. The dynamic 2D population balance equation was solved numerically using CTCN. In the study of Nuttall et al. (1991) only capture and release mechanism effects of the colloid transport model were studied. Colloid agglomeration, pore size exclusion, particle growth, and size distributions were not taken into account in this work. The results of Nuttall et al. indicate that colloid diffusion rate in the direction perpendicular to the flow is an important parameter which was the rate-controlling step in the process of colloids diffusing to the fracture wall and being captured. Diffusion rate of colloids is approximately three orders of magnitude smaller than the diffusion rate for molecular species; consequently, colloids can transport long distances in fractures even with irreversible capture at the rock/water interface. Smaller particles are more likely to come in contact with the rock/water interface but physical capture depends upon the electrokinetic and van der Waals forces. Nuttall et al. also report that under unsaturated conditions, hydrophobic colloids will preferentially collect at the air/water interface and transport at the highest water velocity.

Smith (1992) explored the influence of non-linear sorption on colloid-facilitated radionuclide transport through fractured media. Smith and Degueldre (1993) also explored the result of different solute-colloid sorption mechanisms on radionuclide transport. Smith and Degueldre concluded that the assumption of fast, linear, and reversible radionuclide sorption onto colloids is non-conservative in the prediction of colloid-facilitated radionuclide transport. Smith and Degueldre's work suggests that the time for desorption (days or weeks) exceeds the time for sorption (seconds or minutes) in the radionuclide-colloid interactions. Consequently, it is important to determine the degree of completeness of desorption; irreversible sorption of the radionuclide onto the colloid may be present. If colloids migrate over long distances and are excluded from wall-rock pores due to their size, irreversible sorption would increase the rate of radionuclide transport in the subsurface. Smith and Degueldre concluded that for cases involving irreversible radionuclide-colloid sorption, the transport of radionuclides is strongly dependent on the extent of colloid interaction with the fractures.

Evidence of Colloids and Colloid Transport from Field Studies

Natural Analog Sites

Cigar Lake Uranium Deposit

The colloids ($< 1 \mu\text{m}$) and particulate matter ($> 1 \mu\text{m}$) at the Cigar Lake uranium ore deposit in Canada were characterized by Vilks et al. (1988); the deposit is located at a depth of 400 m and has not been disturbed by mining operations or surface weathering. The ore is surrounded by a clay-rich zone containing iron hydroxides. The clay zone is surrounded by an altered sandstone; the altered sandstone is separated from the surrounding unaltered sandstone by a silica-rich cap, where quartz has filled most of the fractures. Vilks et al. (1988) report that: 1) the total particle concentration in groundwater at Cigar Lake ranges from 0.6 to 261 mg/l. 2) groundwater particles consist of clay minerals, Fe-Si precipitates, organics, rock particles, and drilling products. 3) the natural colloids and suspended particles in the groundwater at Cigar Lake contain significant amounts of U, Th, and ^{226}Ra . 4) uranium dispersion has not been significant beyond the quartz cap. 5) there is no evidence of U migration away from the deposit. 6) radioactive colloid concentrations are low in the overlying sandstone and in the groundwater downgradient from the deposit. 7) no significant migration of colloids and suspended particles away from the uranium ore deposit to the surrounding sandstone has occurred.

Koongarra Uranium Deposit

Groundwater and particles from boreholes at the Koongarra uranium deposit in Northern Australia were characterized by Payne et al. (1992). The chemistry at Koongarra groundwaters is dominated by Mg and bicarbonate, the pH is between 6 and 7.5 and the Eh ranges from 100 to 300 mV. The colloids ($< 1 \mu\text{m}$) and the particles ($> 1 \mu\text{m}$) in the Koongarra groundwaters include clay minerals and fine quartz grains. Iron was observed by Payne et al. as particle coating and as a separate colloidal form. Payne et al. (1992) report that: 1) uranium migrates at Koongarra mostly as dissolved species. 2) thorium and actinium are mostly associated with immobile particles ($> 1 \mu\text{m}$). 3) of the small fraction of Th that passes through a $1 \mu\text{m}$ filter, a large fraction is associated with colloids. 4) actinium appears to be more mobile than Th and is associated with colloids to a greater extent, although in small concentrations. 5) it is possible for trivalent and tetravalent actinides to migrate as colloids away from a nuclear waste repository.

Pocos de Caldas

The characterization of suspended particles and colloids in waters from the Osamu Utsumi mine and Morro de Ferro analog sites at Pocos de Caldas, Brazil was reported by Miekeley et al. (1991). The Osamu Utsumi mine and the Morro de Ferro study sites are located in the center of the Pocos de Caldas Plateau. Uranium is mined by open-cast

methods at Osamu Utsumi. Morro de Ferro is a Th-REE ore body, 14 km from the Osamu Utsumi mine; the Morro de Ferro hill is 140 m above local stream level and is in an advanced state of weathering. The groundwaters at the uranium mine are of the K-Fe-SO₄ type, oxidizing (Eh from 200 to 400 mV), and slightly acidic (pH from 5.4 to 6.1); these groundwaters are the result of weathering of highly leached K-rich rocks. An upward groundwater flow gradient at the mine forces reducing water to ascend into more oxidizing environments. This process is responsible for the formation of ferric oxyhydrates in the suspended particles (> 0.45 μm) and in the colloids (1.5 nm to 0.45 μm) in the groundwaters. The Morro de Ferro ore body is in a much more advanced state of weathering than the Osamu Utsumi mine; the ore body has very high concentrations of Th and REEs in the soil and weathered rocks and much lower concentration of U. At Morro de Ferro, groundwater was sampled at several points down-gradient from the ore body. The gradient extends from a strongly oxidizing (Eh from 450 to 650 mV) to a less oxidizing, unperturbed environment (Eh from 200 to 450 mV). Dissolved organic carbon (DOC) concentrations in the groundwaters from the mine and the ore body range from 1 to 4 mg/l. In shallow waters (in the unsaturated zone) at the Morro de Ferro ore body, DOC concentrations of 10 to 20 ppm were occasionally observed.

Miekeley et al. (1991) report: 1) a colloid concentration at the uranium mine and the ore body of less than 1 mg/l (consisting of Fe(III) oxyhydroxides and humic-like particles in the size range from 1.5 nm to 0.45 μm). 2) small amounts of U and other elements but significant amounts of Th and REEs concentrated in the colloidal phases and suspended particles. 3) high concentrations of colloidal humic-like materials in surface and near-surface waters; this is the reason for the much higher concentrations and proportions of Th and REE in colloidal fractions of organic-rich waters of the Morro de Ferro. 4) solution and colloidal phases in equilibrium with respect to ²³⁴U/²³⁸U isotopic ratios and identical REE distribution patterns for these phases. 5) unfiltered groundwaters with low to moderate concentrations of suspended particles (> 0.45 μm); 0.2 to 0.4 mg/l for the mine and 1 to 5 mg/l for the ore body. 6) no evidence of significant subsurface transport of suspended particles or colloids in either the Osamu Utsumi mine or the Morro de Ferro ore body.

Test Sites

Gorleben Area

Colloids in groundwaters from the Gorleben area, the site for the future German repository, were characterized (Dearlove et al., 1991). The geohydrologic system at Gorleben comprises glacial sand/silt aquifers associated with a Zechstein salt diapir. Dearlove et al. report that: 1) the colloid concentration in the Gorleben groundwaters is 10¹⁷ particles per liter. 2) the bulk of the actinide and lanthanide elements in these groundwaters is associated with humic colloids. 3) the ²³⁴U/²³⁸U ratio indicates that uranium in the colloidal fraction is not in equilibrium with the uranium in solution. 4)

the colloids in the Gorleben aquifer are in the size range from 1.5 to 15 nm. 5) the DOC in these groundwaters are composed of humic and fulvic acids. Kim (1991) reports that: 1) regardless of different redox fronts, Pu and Am are always associated with colloids in the Gorleben groundwaters. 2) the Pu and Am pseudocolloids play an important role in the migration or retention of radionuclides in the subsurface.

Grimsel Test Site

The characterization of colloids flowing in a fracture in the Grimsel Test Site was carried out by Degueudre et al. (1989b). The Grimsel Test Site is considered an example of a granitic/granodioritic far field environment. The site is located in granite in the Swiss Alps about 1750 m above sea level and 450 m below land surface. A colloid concentration of 10^{10} particles per liter in the size range from 0.04 to 1 μm was found in the Grimsel Test Site groundwater. The particles are a mixture of silica and organic material.

Whiteshell Research Area

The Whiteshell Research Area is located in Southern Manitoba, Canada and is an example of fractured granite. Vilks et al. (1991) report that the upper 500 m of the geohydrologic system at this site are connected by three major subhorizontal fracture zones partially interconnected at the surface by near-vertical fractures. At depths greater than 350 m, waters have a salinity between 1 and 15 g/l, a pH of 6.1 to 7.7, and are dominated by Na, Ca, chloride and sulfate. At shallower depths (50 to 350 m) the salinities of the waters range from 0.3 to 1 g/l, the pH of the shallow waters ranges from 7.4 to 8.9, and the waters contain mainly Na, bicarbonate, and to a lesser extent Ca. Both the shallow and deep waters are close to saturation with respect to calcite. Vilks et al. report that the average colloid concentration (in the size range from 10 nm to 0.45 μm) is 0.34 ± 0.34 mg/l and the suspended particle concentration is 1.3 ± 3.0 mg/l. Particles consist of aluminosilicates, carbonates and Fe oxides. Vilks et al. conclude that natural-occurring colloids (in the size range from 10 nm to 0.45 μm) will have a minimal effect on radionuclide transport, provided radionuclide sorption onto colloids is reversible. Vilks et al. point out that if radionuclide sorption onto colloids is irreversible, colloid-facilitated radionuclide transport may be important. If so, then information describing colloid concentrations, colloid stability, and the migration properties of colloids in granite fractures will become necessary.

El Berrocal Site

El Berrocal experimental site is located 92 km southwest of Madrid (Gomez et al., 1992). in a fractured and weathered granitic formation. Uranium-bearing quartz dike/breccia intersects the excavated Berrocal site. Preliminary results indicate: 1) the presence of particles in groundwaters at El Berrocal in the size range from 50 nm to 1 μm . 2) particles mainly consisting of silica, aluminosilicates, oxyhydroxides, and organic

material. 3) dilute, slightly-oxidizing-to-oxidizing groundwaters (Eh of 4 to 379 mV). 4) sulfide colloidal phases in the slightly-oxidizing groundwaters.

Nevada Test Site and Environs

Kingston and Whitbeck (1991) characterized the colloids found in twenty-four springs and wells in central and southern Nevada, in a region underlain by carbonate rocks. The majority of the sites are on or within 50 km of the Nevada Test Site; other sites are located near Hiko and Tonopah, Nevada.

Kingston and Whitbeck report particle concentrations in the following size ranges: 0.03 to 0.1 μm , 0.1 to 0.4 μm , 0.4 to 1 μm , and greater than 1 μm . Kingston and Whitbeck defined colloids as stable particles in suspension in the size range from 1 nm to 1 μm . They concluded that: 1) most of the groundwaters studied have colloid concentrations in the range from 0.28 to 1.35 mg/l; three sites have high colloid concentrations ranging from 6.48 to over 25 mg/l. 2) colloid concentrations are similar regardless of hydrologic setting, aquifer lithology, or geographic location. 3) no obvious correlation exists between water chemistry and colloid concentrations in the waters studied. 4) silica (but not quartz) is present in all the colloids collected; relatively small amounts of clay or zeolite are found in all samples; calcite appeared in some samples but it may be an artifact of the procedures utilized; the organic structures identified in the colloidal fractions are indicative of humic or fulvic acid coating on the mineral colloid surfaces. 5) colloids successfully travel through the subsurface at the Nevada Test Site as indicated by their ubiquitous presence; similar concentrations among the various size ranges may be indicative of groundwater flow at the Nevada Test Site being controlled by faults and fractures. 6) silica colloids can sorb Cs, Co, and Eu; comparison of colloids and tuff sorption distribution coefficients suggests that Eu may preferentially sorb to the colloids rather than to the tuffaceous rocks of the Nevada Test Site.

Water from the well J-13 at the Nevada Test Site was used for particulate analysis. The groundwater from the volcanic units at the Nevada Test Site are dilute sodium bicarbonate waters. The water from the well J-13 has a pH of 6.9 and an Eh of 340 mV. Sodium, calcium, potassium, and magnesium are the cations; bicarbonate, sulfate, chloride, nitrate, and fluoride are the anions in order of decreasing concentration. The other major constituent is silica. Ogard (1987) diverted water from the well J-13 into a mobile laboratory at a rate of ~ 1 l/min. A prefilter was used to remove particles larger than 10 μm prior to filtration of the water through a large stainless steel One-Sevener Nucleopore Filter Assembly which was loaded with seven 0.4 μm membrane filters, mounted in parallel. Approximately one half of the water filtered through this assembly subsequently passed through an Amicon Hollow Fiber Filter system which removes particulates with diameters greater than ~5 nm. A filtration run conducted for 14 days yielded a sediment concentration of the water filtered through a 0.4 μm filter of ~ 2.7×10^{-5} g/l. The amount of material in the fraction filtered through a 5 nm filter was 1% that of the large-size fraction. The particulate fraction in the size range

from 0.4 to 10 μm was dissolved in acid and analyzed; the cations in the fraction (in wt%) are: Si (60), Fe (20), Ca(11), and Al (4). The particulates collected by the hollow fiber system were backflushed with Nanopure water and analyzed; the cations in the smaller-sized fraction (in wt%) are: Na(44), Si(42), Ca(8), and Fe (4). The iron-rich particulates are suspected to be the result of contamination from the steel piping and pumping systems utilized.

Ogard (1987) assessed the importance of particulates in the transport of radionuclides at Yucca Mountain; he based this assessment on the particulate concentration in J-13 water that he reported ($\sim 2.7 \times 10^{-5}$ g/l for particles in the range from 0.4 to 10 μm) and reversible sorption of radionuclides onto colloidal species. Ogard concluded that the particulates in the J-13 well water would have to exhibit a sorption distribution coefficient greater than 4×10^6 ml/g for a given radionuclide in order for pseudocolloids to contribute more than 10% to the total amount of radionuclide migrating through Yucca Mountain. Ogard points out that sorption distribution coefficients of that magnitude have not been observed for the sorption onto tuff of any radionuclide in the high-level waste.

Minai et al. (1992) isolated humic material from water from the J-13 well; the carboxylate group concentration reported was 2.7 meq per g for the fulvic acid fraction and 4.6 meq per g for the humic acid fraction. Minai et al. report that their procedures to isolate the organic fraction were only able to recover 1 - 5% of the total organic component in J-13; they based this information on work by other authors that report the TOC in J-13 water to range from 0.15 to 0.54 ppm.

Field studies of radionuclide migration from underground nuclear tests at the Nevada Test Site have been carried out since 1974. Buddemeier and Hunt (1988) reported the transport of colloidal contaminants in groundwater away from the cavity of the Cheshire event fired on February 14, 1976 with a yield in the 200 to 500 kiloton range. The Cheshire site is on Pahute Mesa. The nuclear test was performed at a depth of 1167 m in a formation consisting of fractured rhyolitic lavas. The pre-shot water level was at a depth of 630 m. Buddemeier and Hunt (1988) conducted filtration and ultrafiltration studies on groundwater samples from the seven-year old cavity of the Cheshire event and from the fractured lava and tuff formation 300 m down-gradient from the cavity. Substantial concentrations of submicrometer colloids and significant radionuclide concentrations were found at both locations. A significant fraction of the radioactivity at both locations was associated with colloidal particles ranging in size down to 3 nm; lanthanide and transition metal radionuclides were completely associated with particulates. Buddemeier and Hunt (1988) concluded that: 1) a strong association exists between colloids and radionuclides. 2) both the dissolved and colloidal radionuclide species migrate through the interconnected fractures.

Shallow Aquifer in a Semiarid Region at Los Alamos

Treated liquid wastes containing traces of Pu and Am are released into Mortandad Canyon, within Los Alamos National Laboratory, NM (Penrose et al., 1990). The shallow alluvium of Mortandad Canyon is composed of sandy to silty clays formed by weathering of volcanic rocks. Penrose et al. (1990) observed detectable amounts of Pu and Am in monitoring wells as far as 3390 m downgradient from the discharge even though laboratory sorption studies predict that the movement of Pu and Am will be limited to less than a few meters. Penrose et al. report that there is very strong evidence that Pu and Am are associated with colloidal materials (in the size range from 25 nm to 0.45 μm) in a way that is effectively irreversible and that colloidal materials can be mobile for great distances.

Potential Sources of Colloids at Yucca Mountain

Moulin and Ouzounian (1992) pointed out that colloids and organic substances can affect the mobility of radionuclides as a result of complexation, sorption, and dissolution/precipitation. Radioactive waste-derived colloids are: degradation colloids, precipitation colloids, and pseudocolloids.

Bates et al. (1993) study the parameters that could affect the reactions of glass waste forms in an unsaturated environment with possible air exchange with adjacent biospheres (typical of what might be expected at Yucca Mountain). Buck et al. (1993) utilized analytical electron microscopy to study colloid generation from nuclear waste glass reactions. Buck et al. demonstrated that colloids are generated during waste glass dissolution and that the colloids generated often contain radioactive elements. High-level waste glass in a nuclear waste repository may be contacted by water vapor, small amounts of sorbed liquid water or flowing water (Bates et al., 1992). Bates et al. (1992) utilized a test method involving dripping water onto a glass-metal assembly, suspended in a vessel; water collected in the bottom of the vessel was filtered to determine whether the actinides Np, Pu, and Am were associated with particulates or dissolved in solution. Bates et al. (1992) reported that 70% of the Np passes through 1 nm filters and can be considered truly dissolved. Over 99% of the Pu and Am in the test groundwater is concentrated in colloidal particles which are fragments of a hydrated layer that spalls from the glass surface during aqueous alteration. Feng et al. (1992) studied the colloids generated from the interaction of high-level nuclear waste glasses with groundwater at 90 °C. The tests (performed by Feng et al.) consisted of immersing powder glass in water from the well J-13. The Teflon test vessel was then tightly sealed and placed in a 90 °C oven. After termination of a test, settling was allowed to occur at room temperature overnight. The glass leachate (after settling) was analyzed for colloids. Feng et al. concluded that waste glass contributes to the formation of colloids by: 1) increasing ionic strength of the groundwater (which leads to nucleation), 2) releasing radionuclides that form pseudocolloids (by sorbing to groundwater colloids), and 3) by spalling fragments of colloidal size from the surface

layer of the reacted glass. Feng et al. report that: 1) the colloids found in the leachate are mainly silicon-rich smectites and uranium silicates, 2) colloids in the leachate agglomerate when the salt concentration is high but the agglomerated colloids can resuspend if dilution takes place, 3) colloids in the leachate agglomerate quickly after the leachate is cooled to room temperature; most of the colloids settle out of the suspension after the leachate has been at ambient temperature for a few days, and 4) the colloids in the leachate are negatively charged between pH 1 and 10.5. Feng et al. inferred from these studies that: 1) in a glass-reaction dominated repository environment, where salt concentrations are likely to be high, the colloid concentration is likely to be low, and the colloid transport of radionuclides will be minimal, 2) if a large amount of groundwater contacts the glass reaction site, the colloids that have settled out of suspension may resuspend and colloid transport may be important, and 3) at ambient temperatures, the colloids may agglomerate quickly and settle out of suspension in a short time.

Real Pu(IV) colloids, produced by the agglomeration of hydrolyzed Pu(IV) ions under acidic conditions have been reported by Hobart et al. (1989) and Triay et al. (1991). Hobart et al. provided evidence that colloidal Pu(IV) is electrochemically reactive and structurally similar to plutonium oxide. Triay et al. reported stable Pu(IV) colloids under acidic conditions in the size range from ~1 nm to 0.4 μm . These Pu(IV) real colloids, generally referred to as Pu(IV) polymers, may not be stable at near-neutral pH values. In addition, the actinide colloids have a positive surface charge and would be expected to attach to tuffs at Yucca Mountain with negative surface charges. However, the formation of actinides pseudocolloids in groundwaters has been reported in numerous studies and reviewed by Kim (1991).

The existence and formation mechanisms of natural colloids at Yucca Mountain which may allow the generation of pseudocolloids at the proposed repository have been studied by Levy (1992). Materials of potential interest include both gels that are still liquid-rich and former gels that have solidified and crystallized. The materials studied by Levy include cores and sidewall samples from drill holes at Yucca Mountain and semi-transparent fluid gel samples from tunnel exposures at Rainier Mesa. Both Yucca Mountain and Rainier Mesa (40 km from Yucca Mountain) consist of ash-flow and bedded tuffs. Levy reports that diagenetic and hydrothermal alteration of volcanic glass are responsible for the genesis and deposition of gels at Yucca Mountain. The principal gel products at Yucca Mountain and Rainier Mesa were heulandite-clinoptilolite, silica minerals, and smectite. Levy (1992) predicts that given the heat generated by the proposed repository (Buscheck and Nitao, 1993) in devitrified Topopah Spring tuff, recharge water or reflux water concentrated by the repository thermal effects may be sufficient to cause local alteration of glass in the underlying vitrophyre and colloid formation.

Kim (1991) pointed out the potential importance of microorganisms as colloids that can bind radionuclides and migrate through the subsurface. Bales et al. (1989) described the utilization of bacteriophage to study transport through sandy soil and fractured tuff. Bales et al. report that: 1) virus particles can travel several meters in sandy aquifers. 2)

the apparent exclusion from 35 to 40% of the pore volume in a granular medium suggests that virus will travel 1.6 to 1.9 times faster than a conservative tracer. 3) results from granular-medium and fractured-tuff experiments illustrate the inability of a soluble conservative tracer to provide estimates for the dispersion and effective porosity applicable to a colloid.

Choppin (1988) pointed out the importance of humic materials on metal ion speciation and behavior in geologic systems at concentrations as low as 0.1 ppm. Minai et al. (1992) measured the binding constant of the humic and fulvic acid fractions in water from the well J-13 for Am(III); they report that these binding constants are similar to those of other aquatic materials. Based on a TOC concentration in J-13 of 0.01 to 0.1 ppm, Minai et al. conclude that the Am-humate complex could be a significant species in J-13 water. Although Minai et al. did not measure any other actinide with the humic material from J-13, they extrapolated from other studies. Uranyl speciation would not be affected in J-13 water unless the TOC is greater than 0.2 ppm. Minai et al. indicate that humic material at ppm levels reduces Pu(VI) and Pu(V) to Pu(IV); consequently Pu present in the V and VI oxidation states would be reduced to the IV state. If the Eh is low enough to allow formation of Pu(III); then Pu speciation would be affected by humics in the same manner as Am(III).

Previous Laboratory Experiments in Support of the Yucca Mountain Site Characterization Project

Thompson (1989) studied the retardation of Pu(IV) real colloid (polymer) and Am(III) through columns made of crushed tuff from Yucca Mountain (in the grain size range from 75 to 500 μm). The columns used for the study were 5 cm long and 0.45 cm in diameter with a porosity of 0.5 to 0.6. The interstitial velocity used for these studies was 150 m/y. The Pu(IV) real colloid used by Thompson for these experiments ranged in size from 50 nm to 0.4 μm . Thompson reports that Pu(IV) real colloid and Am(III) are largely retained by the tuff, with a small fraction of the injected material moving through the columns faster than the tritiated water (used as the conservative tracer).

Rundberg et al. (1989) measured the migration of colloidal polystyrene tracers through a saturated fractured tuff column. The fractured tuff sample was an outcropping from Fran Ridge (near Yucca Mountain). The fractures in this sample were originally filled with calcite; after the fractured tuff sample was encapsulated for tracer elution, the calcite was leached with dilute hydrochloric acid. Transport in this fracture sample was not describable using the cubic law aperture determined from the fracture permeability. In order to fit the elution data for a conservative tracer, adjustment of the fracture aperture was required. Rundberg et al. report that polystyrene colloids with a $\sim 1 \mu\text{m}$ diameter were found to have the lowest filtration coefficient which is in qualitative agreement with the filtration model considered by Rundberg et al.

The relevance of these column studies for the prediction of colloid-facilitated radionuclide transport at Yucca Mountain is difficult to assess. Thompson's experiments were conducted with crushed tuff. Rundberg et al.'s work was conducted using fractures that were severely altered by the addition of dilute hydrochloric acid to dissolve the calcite fillings and using colloids (such as polystyrene spheres) that are not representative of colloids at Yucca Mountain. The small scale of both sets of column experiments is not comparable to the large scales available for colloid filtration at Yucca Mountain.

Future Direction of Colloid Studies in the Yucca Mountain Site Characterization Project

Degueldre (1992) presented a strategy to study the importance of colloid-facilitated radionuclide transport in granitic systems. This strategy was carefully considered in the development of the colloid strategy to assess the importance of colloid-facilitated radionuclide transport at Yucca Mountain. The strategy to assess the importance of colloids at Yucca Mountain to facilitate the transport of radionuclides from the proposed repository to the accessible environment is illustrated in Figure 2. The strategy consists of asking the following questions:

- 1) Will radioactive waste-derived colloids be present at the proposed repository?
- 2) Will these colloids be stable in likely groundwaters?
- 3) Can these colloids migrate over field-scale distances?

The investigations needed to answer the questions in items 1 - 3 are as follows.

Will radioactive waste-derived colloids be present at the proposed repository?

Laboratory experiments like the ones being performed by Bates et al. (1992 and 1993) will address the generation of degradation colloids from high-level waste glass forms. This type of study will provide a degradation colloid concentration source term for repository's performance assessment calculations (PA) which will include the actinide content of the degradation colloids.

The formation of colloids by natural glass alteration in a repository hydrothermal environment will be addressed by natural analog studies at Yucca Mountain. Natural hydrothermal alteration in the cooling pyroclastic deposits 12 to 13 million years ago may be a useful analog to a waste repository environment. Relict colloidal material has been identified among the alteration products in the glassy rocks below the potential repository.

The surface charge of radiocolloids (such as Pu colloids) is positive; consequently, radiocolloids will attach to the tuff at Yucca Mountain which has a negative surface charge at near-neutral pH values and become immobilized. However, the formation of pseudocolloids from the sorption of real actinide colloids onto groundwater colloids is of concern. The generation and properties of real actinide colloids will be studied utilizing the methods presented by Hobart et al. (1989) and Triay et al. (1991).

Addressing the formation of pseudocolloids requires knowledge of the groundwater colloids at Yucca Mountain. In order to address the generation of groundwater colloids at Yucca Mountain, samples will be collected at selected sites in the vicinity of the potential repository block in an attempt to quantify and qualify the presence of inorganic colloids, high- and low-molecular-weight dissolved organic carbon compounds, and selected microorganisms in saturated-zone ground waters. Limitations on uses of data deriving from the samples will be a function of the extent to which samples represent the medium from which they are extracted. This raises fundamental concerns about sample representativity and integrity.

Samples will be collected from discrete intervals isolated by pneumatic packers, generally in uncased boreholes. Interval lengths likely will range between 2 and 20 meters, and will be selected based on borehole televiewer and caliper data. Borehole wall rugosity and fracture distribution and orientation will be primary factors used to determine packer locations. Rates of withdrawal from different intervals will range from about 0.5 to 2 liters per minute, and will be selected to minimize horizontal shear velocities at the borehole wall, in order to preclude or minimize detachment and entrainment of non-suspended particles. Preliminary determination of velocity constraints will begin with information reported by Hunt (1982), Hubbe (1985 a,b), and Ryan (1988). The pump and isolation equipment within the borehole (packers, screens, and adjacent tubing) will be constructed of stainless steel. Tubing used to transport samples up-hole to the mobile laboratory at the well head will be either nylon, polypropylene, or Teflon. Preparation will include efforts to preclude, minimize, or identify sampling-system effects on microbiologic samples.

Sample integrity will be determined by the means used to collect and store raw samples, and by the means used to isolate and/or concentrate colloidal phases. Microbiologic samples will be collected using aseptic procedures. The perceived options assume that pumping and isolation equipment do not deleteriously influence sample quality, and include centrifugation, filtration, and sedimentation. Knowing that filtration methods have the capability to induce data artifacts (Rees, 1990, p. 2777), isolated sequential filtration similar to that carried out by Ogard (1987) can be used to preclude atmospheric influences and enable maintenance of sufficient pressure to satisfactorily prevent CO₂ de-gassing and attendant pH change. This method also is conducive to accumulating relative large masses of particles. Tangential flow filtration is a closed-system method that also can be used to process large volumes and yield particle concentration increases of at least two orders of magnitude. It is conceivable, however, that this re-circulating tangential technique can disaggregate natural particles. An alternative to isolated sampling is an adaptation of the method developed by

Degueldre and Thomi (1986) for pulsed diaultrafiltration under a controlled mixed-gas atmosphere, the CO₂ partial pressure of which is determined using any of several geochemical codes.

Particles will be quantified and/or qualified, as deemed appropriate, using one or a combination of several techniques. If feasible, either absolute inorganic colloid concentrations or size-range concentrations will be determined on site at selected intervals during pumping to provide transient information relative to representativity and final representative concentration data. If this is not possible, periodic samples will be collected during pumping for subsequent separation and/or analysis. Particles as small as 1 nanometer can be filtered from discrete aliquots counted, and size distributions measured using scanning (Degueldre et al., 1989 a,b) or transmission electron microscopy (Gschwend and Reynolds, 1987; Ryan and Gschwend, 1990) and attendant energy dispersive spectroscopy, or atomic force microscopy (Emch et al., 1992; Zenhausern et al., 1992). Phases can also be identified by determination of bulk chemistry of filtered material and perhaps by x-ray diffraction analysis of particles of sufficient size.

Dissolved organic carbon contents of ground waters, and the attendant high- and low-molecular-weight carbon fractions represented generally as humic and fulvic acids, will be quantified and qualified.

The sorption behavior of the actinides (Pu, Am, U, and Np) onto the groundwater colloids to form pseudocolloids will be studied (Vilks and Degueldre, 1991) to determine radionuclide distributions between the colloids and the groundwaters and assess the reversibility of the sorption mechanism of radionuclides onto colloids. Spectroscopy studies will provide supplemental information by identifying the mechanisms of radionuclide sorption onto colloids. Formation of humics or fulvic pseudocolloids will be studied with the actinides and the organic fractions isolated from the saturate-zone colloidal fraction in order to assess the importance of actinide-humate or fulvate species. These studies will yield groundwater colloid concentrations and the capacity of these colloids to carry radionuclides.

2) Will radioactive-waste derived colloids be stable in likely groundwaters?

Given the thermal loads being considered for the proposed repository, elevated temperatures are expected in the near field (Buscheck and Nitao, 1993); consequently, colloids in the near field will not be stable. The stability of degradation colloids as a function of temperature and likely water chemistries in the unsaturated zone will be studied using the colloids generated in the laboratory experiments to address colloid formation at the proposed repository (Bates et al., 1992 and 1993). The stability of radiocolloids, groundwater colloids (silica, zeolites, and clays), and pseudocolloids will be studied as a function of unsaturated- and saturated-zone water chemistry and temperature. The studies will incorporate a range of Ca concentrations representative of the Yucca Mountain vicinity. Degueldre (1992) was able to correlate the

concentrations of colloids in different granitic systems with the Ca concentration of the groundwater at those sites. Even though Kingston and Whitbeck (1991) did not find any correlation of the colloid concentrations at the Nevada Test Site with the groundwater chemistry, it is possible that the correlation exists and that the data of Kingston and Whitbeck is the result of particulate contamination during sampling.

3) Can radioactive-waste derived colloids migrate over field-scale distances without being removed by filtration?

The mobility of the colloids through the medium at Yucca Mountain will be addressed by conducting transport experiments. Laboratory-scale column experiments which involve eluting well characterized colloids (such as polystyrene spheres), degradation colloids, radiocolloids, and pseudocolloids through porous and fractured tuff columns will be used to validate a transport code capable of describing colloid transport (such as FEHM or CTCN). These studies will yield attachment/detachment parameters for colloids migrating through tuff which can be used by performance assessment calculations.

Elution of colloids through a large lysimeter filled with porous media and blocks (~ 1 m³) of fractured tuff will be performed to address the gap between the laboratory and field scales.

Field-scale colloid transport in unsaturated, fractured tuff will be studied (Hunt, 1993). Hunt's proposal for such a study involves weapons tests at the Nevada Test Site which could provide a worst-case scenario to evaluate whether radionuclides leached beneath a weapons test fired above the water table. Hunt (1993) points out that a nuclear weapons test is similar to a high level nuclear waste repository. A weapons test emplaces long-lived radionuclides within a fractured formation and within molten glass. The heat is gradually diffused away and water enters the test cavity (first as a vapor and then as a condensed liquid partially coating the surfaces). This water would promote glass and mineral weathering. The weapons test can also produce a surface crater that will act as a collection point for precipitation and accelerate infiltration. Hunt (1993) proposes the utilization of a test site where: 1) the weapons cavity is at least 100 meters above the water table (so that enough unsaturated zone space exists to study beneath the cavity), 2) the nuclear weapons test would have produced a surface depression that would accelerate and concentrate water infiltration, 3) the test should be at least 10 years old to allow for heat dissipation and water infiltration. Sampling the rock around and beneath this test would provide data representing a worst-case scenario for Yucca Mountain with an unpackaged waste-containing glass subjected to water and infiltration through partially saturated freshly-fractured tuff.

Field-scale colloid transport in the saturated zone will be studied by injecting polystyrene microspheres during cross-hole hydraulic testing at a well complex at Yucca Mountain (C-Wells). This effort will provide an opportunity to study colloid transport through saturated, fractured tuff; and will simulate a scenario involving

formation of pseudocolloids that reach the groundwater table at Yucca Mountain. The concept of the C-Wells field experiments is to inject various tracers (including well-characterized colloids) into the saturated zone via an injection well and observe the appearance of these tracers in sampling wells at downgradient locations.

The field experiments will allow the validation of a transport code to predict colloid transport through fractured tuff at large scales. If validation results are satisfactory, this code can be used to perform sensitivity analyses to identify the information that needs to be considered in performance assessment to address the importance of colloid-facilitated radionuclide transport from the proposed repository at Yucca Mountain.

In summary, available information on colloid transport is not sufficient to conclude that colloids will not be able to carry radionuclides from a repository to the accessible environment at Yucca Mountain. In order for colloids to facilitate radionuclide transport at Yucca Mountain, they must be present in stable suspensions in sufficient quantities, the radionuclides must be associated with the colloids, and the colloids must be transported over field-scale distances. Consequently, the strategy developed addresses these three main issues which are critical to assessing the importance of colloid-facilitated radionuclide transport at a nuclear waste repository.

References

- Bales, R. C., C. P. Gerba, G. H. Grondin, and S. L. Jensen (1989). "Bacteriophage Transport in Sandy Soil and Fractured Tuff," *Applied and Environmental Microbiology*, Vol. 55, No. 8, 2061-2067. NNA.930607.0065
- Bates, J. K., J. P. Bardley, A. Teetsov, C. R. Bradley, and M. Buchholtz ten Brink (1992). "Colloid Formation During Waste Form Reaction: Implications for Nuclear Waste Disposal," *Science*, Vol. 256, 649-651. NNA.920416.0050
- Bates, J. K., W. L. Bourcier, C. R. Bradley, E. C. buck, J. C. Cunnane, N. L. Dietz, W. L. Ebert, J. W. Emery, R. C. Ewing, X. Feng, T. J. Gerding, M. Gong, J. C. Hoh, H. Li, J. J. Mazer, L. E. Morgan, L. Newton, J. K. Nielsen, B. L. Phillips, M. Tomozawa, L. Wang, and d. J. Wronkiewicz (1993). "ANL Technical Support Program for DOE Environmental Restoration and Waste Management," Annual Report October 1991 - September 1992 ANL-93/13. NNA.930907.0056
- Buck, E. C., J. K. Bates, J. C. Cunnane, W. L. Ebert, X. Feng, and D. J. Wronkiewicz (1993). "Analytical Electron Microscopy Study of Colloids from Nuclear Waste Glass," *Mat. Res. Soc. Sym. Proc.* Vol. 294, 199-206. NNA.930907.0053
- Buddemeier, R. W., and J. R. Hunt (1988). "Transport of Colloidal Contaminants in Groundwater," *Applied Geochemistry*, Vol. 3, No. 5, 535-548. NNA.930701.0051
- Buscheck, T. A. and J. J. Nitao (1993). "The Analysis of Repository-Heat-Driven Hydrothermal Flow at Yucca Mountain," to appear in Proceedings of the 4th Annual International High-Level Waste Management Conference, April 26-30, 1993, Las Vegas, NV. NNA.930315.0012
- Choppin, G. R. (1988). "Humics and Radionuclide Migration," *Radiochimica Acta* 44/45, 23-28. NNA.930607.0066
- Dearlove, J. P. L., G. Longworth, M. Ivanovich, J. I. Kim, B. Delakowitz, and P. Zeh (1991). "A Study of Groundwater-Colloids and their Geochemical Interactions with Natural Radionuclides in Gorleben Aquifer Systems," *Radiochimica Acta*, 52/53, 83-89. NNA.830607.0067
- Degueldre, C. and H. Thomi (1986). "Réalisation d'une cellule de dialultrafiltration a injection pulsée," Paul Scherrer Institute Technical Memo TM-42-86-37.
- Degueldre, C., G. Longworth, V. Moulin, P. Vilks, C. Ross, G. Bidoglio, A. Cremers, J. Kim, J. Pieri, J. Ramsay, B. Salibu, and U. Vuorinen (1989 a). "Grimsel Colloid Exercise: An International Intercomparison Exercise on the Sampling and Characterization of Groundwater Colloids," Paul Scherrer Institute Internal Report TM-36. NNA.930625.0034

- Degueldre, C., B. Baeyens, W. Goerlich, J. Riga, J. Verbist, and P. Stadelmann (1989 b). "Colloids in Water from a Subsurface Fracture in Granitic Rock, Grimsel Test Site, Switzerland," *Geochimica et Cosmochimica Acta*, Vol. 53, 603-610. NNA.930607.0068
- Degueldre, C. (1990). "Grimsel Colloid Exercise," Final Report EUR 12660 EN, Luxembourg. NNA.930625.0034
- Degueldre C. (1992). "Colloid Properties in Granitic Groundwater Systems, with Emphasis on the Impact on Safety Assessment of a Radioactive Waste Repository," to appear in Proceedings of the 1992 Material Research Society Fall Meeting, November 30 - December 4, 1992, Boston, MA. NNA.830807.0069
- Emch, R., F. Zenhausern, M. Jobin, M. Taborelli, and P. Descouts (1992). "Morphological Difference between Fibronectin Sprayed on Mica and on PMMA," in *Ultramicroscopy 1992, Proceedings of the Sixth International Conference on Scanning Tunneling Microscopy and Related Techniques*.
- Feng, X., E. C. Buck, C. Mertz, J. K. Bates, and J. C. Cunnane (1993). "Study on the Colloids Generated from Testing of High-Level Nuclear Waste Glasses," Proceedings of the Symposium on Waste Management on Tucson, AZ, February 28 - March 4, 1993, Vol. 2 1015-1021. NNA.930907.0054
- Gomez, P, M. J. Turrero, V. Moulin, and M. C. Magonthier (1992). "Characterization of Natural Colloids in Groundwaters of El Berrocal, Spain," *Water-Rock Interaction, Balkema, Rotterdam*, 797-800. NNA.830607.0071
- Gschwend, P.M. and M.D. Reynolds (1987). "Monodisperse Ferrous Phosphate Colloids in an Anoxic Groundwater Plume," *J. Contam. Hydrol.*, 113(1): 232-240.
- Hobart, D. E. , D. E. Morris, P. D. Palmer, and T. W. Newton (1989). "Formation, Characterization and Stability of Plutonium (IV) Colloid: A progress Report," in *Proceedings of Nuclear Waste Isolation in the Unsaturated Zone, FOCUS '89*, September 17-21, 1989, Las Vegas, Nevada, pp 118-124. NNA.890815.0254
- Hubbe, MA. (1985 a). "Detachment of Colloidal Hydrous Oxide Spheres from Flat Solids Exposed to Flow – 1. Experimental System," *Colloids and Surfaces*, 16: 227-248.
- Hubbe, MA. (1985 b). "Detachment of Colloidal Hydrous Oxide Spheres from Flat Solids Exposed to Flow – 2. Mechanisms of Release," *Colloids and Surfaces*, 16: 249-270.
- Hunt, J. R. (1982). "Particle Dynamics in Seawater: Implications for Predicting the Fate of Discharged Particles," *Environ. Sci. Technol.*, 16: 303-309.
- Hunt, J. R. (1993). Personal Communication.

Jain, R. (1991). "CTCN: A User's Manual," MS Thesis, Chemical and Nuclear Engineering Department, University of New Mexico, Albuquerque, NM. NNA.93071.0052

Kessler, J. H. and J. R. Hunt (1993). "Open Channels in Fractures Maintained by Deposition and Erosion of Colloids," to appear in Proceedings of the 1993 International High Level Waste Management Conference, Las Vegas, NV, April 26 - 30, 1993. NNA.930607.0072

Kingston, W. L., and M. Whitbeck (July 1991). "Characterization of Colloids Found in Various Groundwaters Environments in Central and Southern Nevada," Water Resources Center Publication #45083. NNA.930607.0073

Kim, J. I. (1991). "Actinide Colloid Generation in Groundwater," *Radiochimica Acta*, 52/53, 71-81. NNA.930625.0030

Levy, S. S. (1992). "Natural Gels in the Yucca Mountain area, Nevada, USA," *Applied Clay Science*, 7, 79-85. NNA.830607.0074

McCarthy, J. F. and J. M. Zachara (1989). "Subsurface Transport of Contaminants," *Environmental Science and Technology*, Vol. 22, No. 5, 496-502. NNA.830625.0032

McDowell-Boyer, L. M., J. R. Hunt, and N. Sitar (1986). "Particle Transport through Porous Media," *Water Resources and Research*, Vol. 22, No. 13, 1901-1921. NNA.900302.0036

Meijer A. 1992. "A Strategy for the Derivation and Use of Sorption Coefficients in Performance Assessment Calculations for the Yucca Mountain Site," in Proceedings of the DOE/Yucca Mountain Site Characterization Project Radionuclide Adsorption Workshop at Los Alamos National Laboratory, September 11-12, 1990, Los Alamos National Laboratory Report, LA-12325-C, pp 9-36. NNA.920819.0077

Miekeley, N., H. Coutinho de Jesus, C. L. Porto da Silveira, and C. Degueldre (January 1991). "Chemical and Physical Characterization of Suspended Particles and Colloids in Waters from the Osamu Utsumi and Morro de Ferro Analog Study Sites, Pocos de Caldas, Brazil," SKB Technical Report 90-18, Stockholm, Sweden. NNA.930625.0033

Minai, Y., G. R. Choppin, and D. H. Sisson (1992). "Humic Material in Well Water from the Nevada Test Site," *Radiochimica Acta*, 56, 195-199, (and references therein). NNA.930607.0076

Moulin, V. and G. Ouzounian (1992). "Role of Colloids and Humic Substances in the Transport of Radio-elements through the Geosphere," *Applied Geochemistry*, Supplemental Issue No. 1, 179-186. NNA.930607.0077

Nuttall, H. E., R. Jain, and Y. Fertelli (1991). "Radiocolloid Transport in Saturated and Unsaturated Fractures," in Proceedings of the 2nd Annual International Conference on High Level Radioactive Waste Management, Las Vegas, NV, April 28 - May 3, 1991. NNA.930625.0031

Ogard, A. (February, 1987). "Importance of Radionuclide Transport by Particulates Entrained in Flowing Groundwaters," in Groundwater Chemistry at Yucca Mountain, Nevada, and Vicinity, Los Alamos National Laboratory, LA-10929-MS, Los Alamos, NV. NNA.830607.0078

Payne, T. E., R. Edis, and T. Seo (1992). "Radionuclide Transport by Groundwater Colloids at the Koongarra Uranium Deposit," *Material Research Society Symposium Proceedings*, Vol. 257, 481 - 488. NNA.930607.0079

Penrose, W. R., W. L. Polzer, E. H. Essington, D. M. Nelson, and K. A. Orlandini (1990). "Mobility of Plutonium and Americium through a Shallow Aquifer in a Semiarid Region," *Environmental Science and Technology*, 24, 228-234. NNA.830607.0058

Ramsay, J. D. F. (1988). "The Role of Colloids in the Release of Radionuclides from Nuclear Waste," *Radiochimica Acta*, 44/45, 165-170. NNA.930701.0050

Rees, T. F. (1990). "Comparison of Photon Correlation Spectroscopy with Photosedimentation Analysis for the Determination of Aqueous Colloid Size Distributions," *Water Resour. Res.*, 26(11): 2777-2781.

Rundberg, R. S., A. J. Mitchell, M. A. Ott, J. L. Thompson, and I. R. Triay (1989). "Laboratory Studies of Radionuclide Migration in Tuff," in Proceedings of Nuclear Waste Isolation in the Unsaturated Zone, FOCUS '89, September 17-21, 1989, Las Vegas, Nevada, pp 248-255. NNA.891207.0090

Ryan, J. J., Jr. (1988). "Groundwater Colloids in Two Atlantic Coastal Plain Aquifers: Colloid Formation and Stability," Master's thesis, Massachusetts Institute of Technology.

Ryan, J. J., Jr. and P.M. Geschwend (1990). "Colloid Mobilization in Two Atlantic Coastal Plain Aquifers," *Water Resour. Res.*, 26(2): 307-322.

Smith, P. A. (1992). "The Influence of Non-Linear Sorption on Colloid Facilitated Radionuclide Transport Through Fractured Media," to appear in Proceedings of the 1992 Material Research Society Fall Meeting, November 30 - December 4, 1992, Boston, MA. NNA.930607.0059

Smith, P. A. and C. Degueldre (1993). "Colloid-Facilitated Transport of Radionuclides through Fractured Media." to appear in the *Journal of Contaminant Hydrology*. NNA.930607.0064

Thompson, J. L. (1989). "Actinide Behavior on Crushed Rock Columns," *Journal of Radioanalytical and Nuclear Chemistry*, Vol. 130, No. 2, 353-364. NNA.920131.0401

Triay, I. R., D. E. Hobart, A. J. Mitchell, T. W. Newton, M. A. Ott, P. D. Palmer, R. S. Rundberg, and J. L. Thompson (1991). "Size Determinations of Plutonium Colloids Using Autocorrelation Photon Spectroscopy," *Radiochimica Acta* 52/53, 127-131. NNA. 930607.0060

Vilks, P., J. J. Cramer, T. A. Shewchuk, and J. P. A. Larocque (1988). "Colloid and Particulate Matter Studies in the Cigar Lake Natural-Analog Program," *Radiochimica Acta*, 44/45, 305-310. NNA.930607.0061

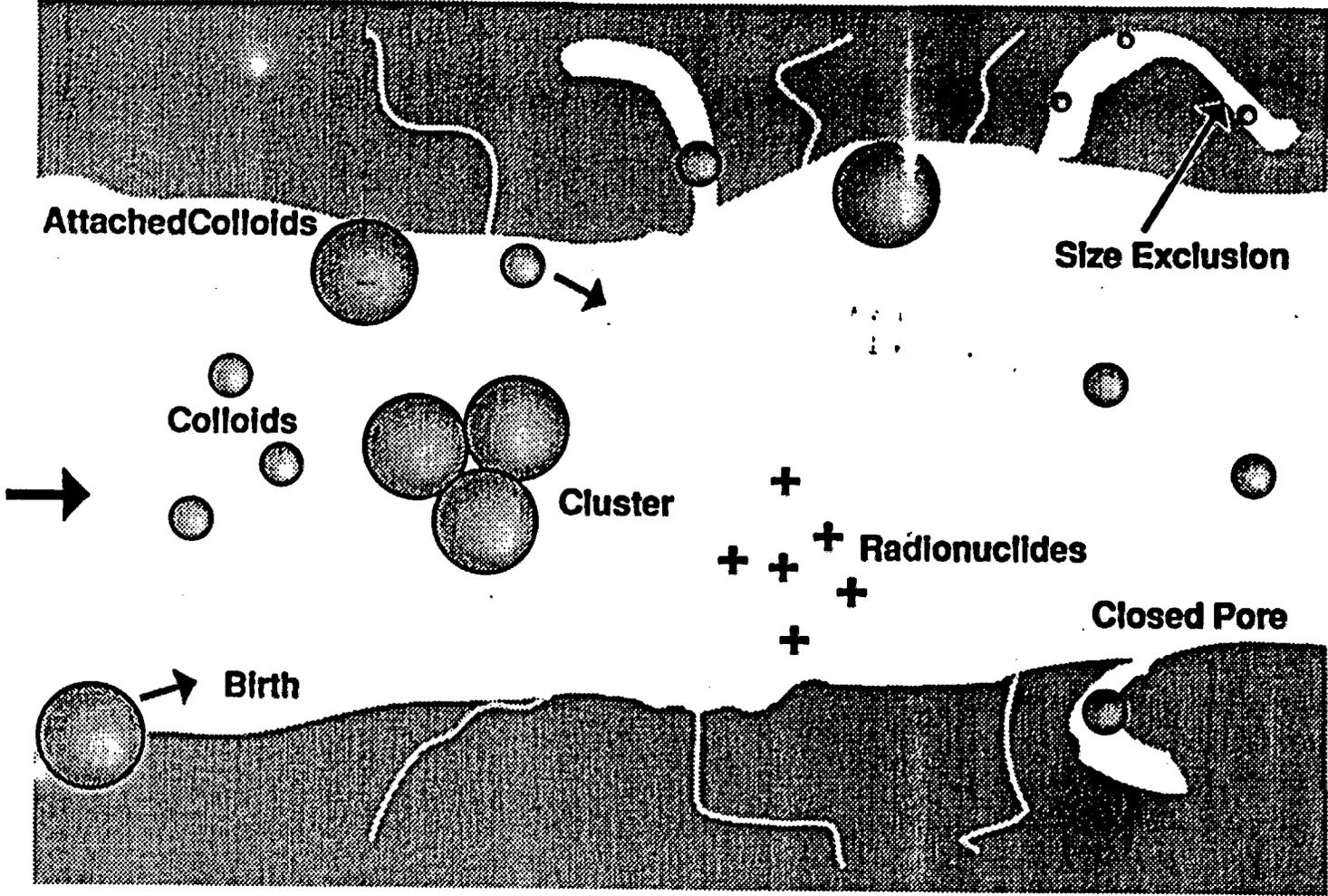
Vilks, P., and C. Degueldre (1991). "Sorption Behavior of ^{85}Sr , ^{131}I , and ^{137}Cs on Colloids and Suspended Particles from the Grimsel Test Site, Switzerland," *Applied Geochemistry*, Vol. 6, 553-563. NNA.930607.0063

Vilks, P., H. G. Miller, and D. C. Doern (1991). "Natural Colloids and Suspended Particles in the Whiteshell Research Area and Their potential Effect on Radiocolloid Formation." *Applied Geochemistry*, Vol. 6, 565-574. NNA.930607.0062

Zenhausern, F., M. Adrian, R. Emch, M. Tadorelli, J. Jobin, and D. Descouts (1992). "Scanning Force Microscopy and Cryo-electron Microscopy of Tobacco Mosaic Virus as a Test Specimen," in *Ultramicroscopy 1992, Proceedings of the Sixth International Conference on Scanning Tunneling Microscopy and Related Techniques*.

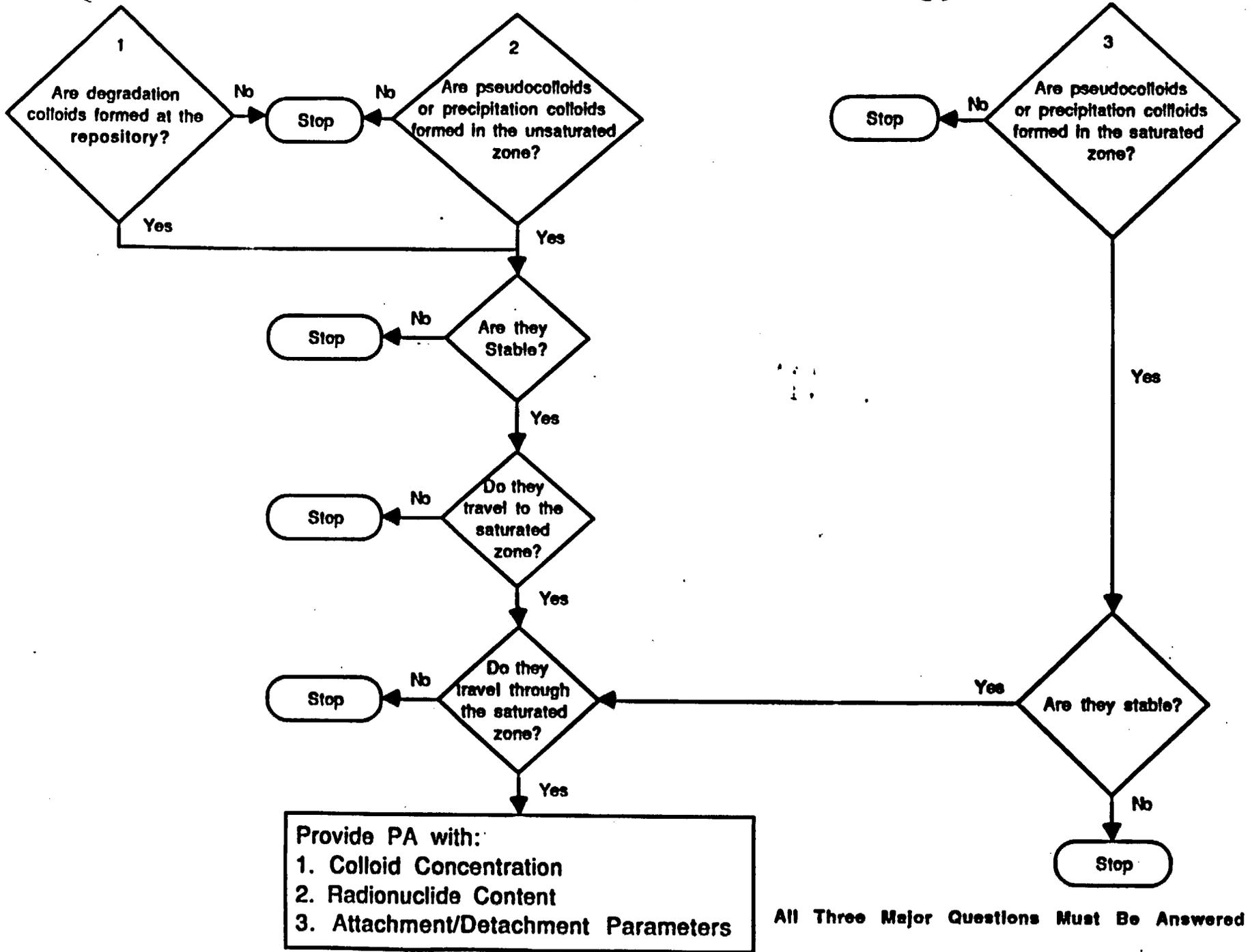
Figure 1: Colloid Processes

Rock Matrix



Rock Matrix

FIGURE 2: YMP Colloid Strategy



Meeting Summary of the Yucca Mountain Site Characterization Project Colloid Workshop

May 3-5, 1993
Santa Fe, New Mexico

This workshop was sponsored by the Yucca Mountain Site Characterization Project (YMP) in an effort to focus attention on the issue of potential colloid transport of radionuclides in the groundwater at Yucca Mountain. It provided an opportunity for the YMP (DOE and participants) and an international body of researchers and other interested parties to: 1) integrate the present state of understanding regarding the importance of colloids in radionuclide transport at Yucca Mountain and other sites, 2) receive expert input into the necessary tests to characterize the presence of colloids, and 3) develop, present, and receive comment on the YMP's strategy to address potential colloid transport of radionuclides.

Each morning and afternoon, a series of technical presentations was given. These sessions were followed by panel discussions. Selected comments and questions from these panel discussions are presented. Panel members for each session are listed, although important questions or comments from all attendees are reported.

The workshop began with a welcome by Julie Canepa, LANL, and a statement of the workshop goals was given by Ardyth Simmons, DOE. The purpose of the workshop was to address the issue of whether colloids will significantly increase radionuclide release to the accessible environment at Yucca Mountain, and if the answer is "possibly" or "yes", to obtain guidance for colloid characterization. In addressing the issue for Yucca Mountain, the workshop attempted to answer the following questions: 1) how can we bound the problem?; 2) what data are available?; 3) what types of colloids exist at Yucca Mountain?; 4) how can we sample colloids?, and 5) how can we characterize colloidal transport at Yucca Mountain?

MONDAY MORNING, MAY 3, 1993

This session was intended to address the question: *Can we bound the potential significance of colloid transport at Yucca Mountain?* On the basis of the presentations and subsequent panel discussion, it appears that mathematical models either exist or can be developed readily to answer this question, however not enough is known about the nature, concentration, and behavior of colloids at Yucca Mountain to provide adequate input to models. This suggests that substantial progress must be made in quantifying and characterizing colloid behavior in general, and specifically at Yucca Mountain, prior to adequately modeling colloid transport for performance assessment calculations..

M. Wilson and M. Siegel, SNL; J. H. Gauthier, SPECTRA Res. Inst.: Colloids: A Performance Assessment Perspective.

ENCLOSURE 2

Performance assesment (PA) is defined as a comparison of predicted repository performance measured against applicable regulatory limits, primarily those of the EPA. PA is essentially a probabilistic effort in which EPA release limits are treated as a random variable for which a probability distribution is determined for a given set of input parameters.

Given that colloids could contribute to release of radionuclides to the accessible environment by groundwater flow, the repository was modelled as six hypothetical one-dimensional stratigraphic columns, including a composite porosity model consistent with lithology. These six columns subsequently fed into one transport column in the saturated zone. The model included Engineered Barrier System elements such as a thermal "dry out" period of 300-1300 years, a container lifetime of 500-10,000 years, advective and diffusive releases, and solubility-limited mobilization. Important transport parameters included advective-dispersive transport, advective and diffusive coupling between the matrix and fracture during transport, and adsorptive (K_d) retardation. The model is believed to employ conservative parameter choices to place an upper bound on expected releases.

The results of transport models indicate that releases of Pu and Am could exceed EPA limits in cases where there is release from the EBS or where there is no sorption or diffusion into the geologic barrier. The important question is how colloids may contribute to release in such cases. Iteratively incorporating colloids into the model depends on the surface area of the colloids, the amount of material sorbed onto them, and the fraction of radionuclides transported on the colloids. Neglecting sorption onto wallrocks and assuming irreversible sorption makes the model conservative. Using colloid concentrations from Ogard (1987) in the model does not result in unacceptable release; however, concentrations reported by Kingston and Whitbeck (1991) could result in radionuclide releases in excess of EPA limits.

In order for the relative importance of colloids to the release of radionuclides to be properly understood, PA modelers need answers to the following questions:

1. What are colloid concentrations at Yucca Mountain, and will they be increased by repository construction, EBS degradation, or future climate changes?
2. Will the effective Pu and Am solubilities be higher because of colloid formation or other near-field conditions?
3. Will Pu and Am sorb preferentially to colloids or will most sorb to immobile rock?
4. Is sorption to colloids reversible or irreversible?
5. Do we need to worry about radiocolloids in addition to pseudocolloids?
6. Is matrix diffusion an effective retardation mechanism for colloids or are they excluded from the matrix?
7. Can colloids travel great distances at Yucca Mountain without being filtered?

H. E. Nuttall, UNM: Colloid Transport Calculations With CTCN.

Modeling colloid transportation with CTCN (Colloid Transport Calculation Nuclear) involves keeping track with numerous parameters such as the birth and extinction of colloids, attachment and detachment of colloids from the wallrock, agglomeration of colloids, adsorption and desorption of radionuclides from colloids, the decay of radionuclides on or within a colloid, and colloid size and charge. Realistic input values for these colloidal properties is crucial in colloid transport calculations, and allows the sensitivity of individual parameters to be tested. The code employs a population balance approach.

The model approximates fracture flow by employing tubes or plates in the calculation. An advantage to the code is that it also permits calculation of 2-d and 3-d models as well as colloid transport in unsaturated media. This is done by assuming that water is wetted to the rock surface as a film of finite width less than the fracture aperture. Experiments have proved important in verifying the code as well as determining the electrostatic charge on colloids as input to the model.

CTCN will be employed in the future at Yucca Mountain to consider the following:

1. Using the code to perform bounding calculations of radionuclide release.
2. Using hydrologic data to investigate colloid transport in the unsaturated zone taking into account the lithology of the repository horizon (Topopah Spring lower non-lithophysal zone), the basal vitrophyre, the nonwelded base, and the zeolitic tuffs of the Calico Hills unit.
3. Using hydrologic data to investigate colloid transport in the saturated zone taking into account the fracture network of the tuff aquifer.
4. Testing the levels of colloid retardation using first order kinetics.
5. Investigating the sensitivity of colloid transport to variations in parameters.

Y. Hwang, Korea's Atom. Ener. Res. Inst.; P.L. Chambre⁹ and T.H. Pigford, UC; and W.W.-L. Lee, Env. Eval. Grp.: Some Models of Colloid Generation and Transport.

The governing equations exist to predict, either by analytical or numerical means, the migration of colloids in terms of advection, diffusion, and filtration in saturated porous and fractured rock. In particular, filtration is an especially important parameter which must be measured. The model suggested that pseudocolloids are too large to diffuse into rock. Approximately ten parameters must be measured to quantify the concentration of pseudocolloids and solute. What remains to be done are laboratory and field scale experiments to quantify filtration, sorption, and diffusion coefficients as input parameters to mathematical models for performance assessment.

Summary of Important Comments Made During the Panel Discussion: (Panel Members: Mike Wilson, Eric Nuttall, Bill Lee, Bruce Robinson)

•Bruce Robinson: It is important to simplify the problem for performance assessment

calculations. Treat colloids as a dissolved species and model as a series of simultaneous chemical reactions using existing flow and transport codes.

•Eric Nuttall: The simplifications need to be validated. Existing codes can be used to perform bounding calculations and determine what parameters are important. The saturated and unsaturated zones need to be modeled separately. The chemistry of rock-water interactions and their effects on colloid generation needs to be understood.

•Bill Lee: Mathematical models are more advanced than our understanding of colloids. If colloids do not migrate in the vadose zone or are filtered, the problem need not be considered further.

•Mike Wilson and Bruce Robinson: It would be beneficial at this point to use existing codes to perform sensitivity tests. PA could now add a parameter like diffusion coefficient and assign a probability distribution as a bounding calculation.

•Eric Nuttall: Bounding calculations may help focus the experimental program.

•Julie Canepa: It appears that our computational ability has exceeded available data as input. Definitive performance assessment will have to be based on data yet to be gathered from both laboratory and field experiments.

MONDAY AFTERNOON, MAY 3, 1993

This session was intended to address the questions: 1) *Do we have sufficient data to establish an upper limit on the amount of suspended solids in the groundwater at Yucca Mountain?* 2) *What is the most likely nature of colloids in the groundwater at Yucca Mountain?* and 3) *How should future colloid sampling studies be conducted?* On the basis of the presentations and subsequent panel discussion, the answer to the first question is no. The answer to the second question is that much more work needs to be done to characterize the nature of the colloids. The answer to the third question is that proper sampling of groundwater for colloids is a difficult task. Many parameters need to be considered in order to properly sample and preserve colloid-laden waters.

G. Choppin, FSU: Humic Materials in Well J-13 Water.

Well J-13 water contains on the order of 0.15 ppm organic matter, some fraction of which are humic and fulvic acids. These materials strongly complex with actinide species. For example, the UO_2 -humic acid: UO_2^{2+} ratio in dilute aqueous solutions is on the order of 500-5000. Given that these organic macromolecules may exist as colloids themselves or as coatings on mineral colloids has obvious implications for radionuclide transport. In addition, humic acids are strong reducing agents.

Humic materials were separated from 3000 gallons of well J-13 water to produce approximately 60 mg of humic acid and 15 mg of fulvic acid, representing an estimated 1-5% recovery. Various spectroscopic analyses indicated that the recovered material was similar in character to aquatic humic material rather than humic acids found in soils.

The speciation of Am with the humic material was calculated. The results indicate a strong tendency for Am to complex with the organic material (Am-humic acid fraction=1).

especially in Ca^{2+} poor waters. In the presence of Ca^{2+} , Am strongly complexes with humic materials at pH 6.9 (0.93), but at higher pH (8.2) partitions in subequal proportions with AmCO_3 (approx 0.42 each).

The nature and presence of humic acids present the following conclusions. First, the speciation of Am could be greatly affected in humic laden waters, especially at $\text{pH} < 7$ and low Ca^{2+} abundances. Second, UO_2^{2+} partitioning and transport will be affected for waters with total organic carbon contents greater than about 0.2 ppm, approximately that concentration in J-13 water. Third, $\text{Pu}^{5+,6+}$ will be reduced to Pu^{4+} by the presence of humic acid. Finally, the levels of humic material found in J-13 water may interact with silicate material, including silicate colloids, to a significant extent. This may enhance the ability of pseudocolloids to adsorb radionuclides. On the other hand, this may also increase the sorption of radionuclides to the rock.

J. F. Kerrisk and A. Ogard, LANL: Particulate Material in Well J-13 Water.

This study attempts to address the potential for significant radionuclide transport by pseudocolloids in flowing groundwater beneath Yucca Mountain. Well J-13 is favorable for study as it was established in 1963 and is routinely pumped. In addition, it is close to Yucca Mountain and the water is produced from the Topopah Spring Member of the Paintbrush Tuff.

A large quantity of water (9300 l) was membrane filtered into several size fractions between 0.4 and 10 μm , and 0.25 g of particulate material were recovered for a concentration of 2.7×10^5 g/l. A hollow fiber filter captured 0.0025 g of colloids between 0.4 μm and 5 nm from 5300 l of water for a concentration of approximately 5×10^7 g/l. The colloidal material was composed of subequal proportions of Si and Fe (about 40% each) and less than 10% Al, Ca, and Na. There is a strong possibility that a substantial portion of the Fe is derived from the pumping system in the well. If so, the colloid concentration is substantially less than that reported.

The primary conclusion of this study is that at the observed concentration of colloids and particulate matter in J-13, radionuclides would have to have an extreme affinity (sorption coefficients of 10^6 or greater) in order for particulates to transport significant quantities of radioactive material as pseudocolloids. This conclusion also requires that sorption to groundwater colloids to form pseudocolloids be much more effective than sorption to rock beneath the repository in order for colloid facilitated transport to be a problem. The question remains, however, whether J-13 water is representative of groundwater beneath the repository and what the true sorption ratios of radionuclides onto those particulates are.

M. Whitbeck, DRI: Occurrence, Composition, and Properties of Colloidal Particles at the NTS.

Colloids are of potential significance in nuclear waste isolation because they represent

mobile binding sites that compete with fixed sites on the rock matrix. The size exclusion principle also suggests that colloids may facilitate radionuclide transport at an accelerated rate over the mean groundwater velocity. It is difficult to overemphasize the importance of the physical and chemical properties of colloid surfaces in an attempt to predict colloid behavior. Properties such as surface charge, complexation, and double layer formation are important parameters in any colloid model.

The objectives of the analytical portion of this study were to collect groundwater samples from a number of different locations (23) at the Nevada Test Site in order to characterize the colloids on a regional scale. Subsequently, the colloids in the groundwater were characterized in terms of their mass abundance and chemical composition by size fraction. Water samples were subjected to pressure cell filtration to separate 1 to 0.03 μm size fractions and size exclusion chromatography separated 20-2 nm fractions. Infrared spectroscopy was then employed to analyze the particles. Mass distributions of filtered samples in mg/l are given below. These data indicate that, on average, there are subequal concentrations of all colloid size fractions in NTS waters, although the large values of the standard deviations indicate the very wide spread in colloid concentrations. Size exclusion peaks of several wells and springs were typically in the 15 - >20 nm range.

Size μm	mean concentration mg/l	1 σ	number of samples
>1	0.48	0.87	22
1 - 0.4	0.47	1.2	22
0.4 - 0.1	0.37	.88	21
0.1 - 0.03	0.33	.36	21

Infrared spectroscopy indicates that the colloids are dominantly silicates with some indication of clay particles at the 1 μm size range. In addition, the Nevada Test Site waters contain about 0.1 ppm total organic carbon, and there are indications of the presence of aliphatic carboxylate, consistent with humic acids. This may be an indication that particles may be coated with organic materials. In regards to surface chemistry, colloids may be more appropriately described by a gel model than a solid-double layer model with an accompanying reduced effective potential and surface complexation.

In summary, total colloid concentrations are on the order of 0.5 mg/l, and seem to have the properties of silica gels with some clay, quartz, and calcite being present. Organic coatings on colloids present in the water have the potential to alter the characteristics of the colloids by affecting their ability to coagulate, affecting their mobility, and affecting their ability to bind contaminants to their surfaces.

B.E. Viani and S.I. Martin, LLNL; M. ten Brink, USGS: Characterization of Inorganic Colloids From Some NTS Well Waters.

In order to characterize colloids from four wells (UE-25 J-13, UE-19c, UE-20n-1, and UE-5c) at NTS, samples were collected after purging. Water was filtered to determine colloidal mass, phases were identified by x-ray diffraction (XRD) and selected area electron diffraction (SAED), and individual compositions were determined by energy dispersive x-ray techniques. Colloid concentrations were observed to be on the order of 1 - 5 mg/l from four wells, and are primarily inorganic. In addition, the colloids represent only 1 - 2% of the total dissolved solids in the waters. Most are Fe and Si-oxides, layered silicates, silica polymorphs, exotic material, or were unstable in the analytical apparatus. The presence of "exotic" colloids indicates possible contamination of the samples.

Transmission electron microscopy (TEM) was employed for individual phase identification. In general, it appears that the mineralogy of the colloids mimics that of the country rock surrounding the well from which they were derived. TEM of colloids in the wells indicated the presence of 1) iron oxides, layer silicates, and Ca-rich phases in J-13, 2) iron oxides, and layer silicates in UE-5c, and 3) SiO₂ polymorphs in UE-19c. Flow through experiments of fractured Topopah Spring tuff produced colloids identifiable by TEM. This indicates that this technique may be used to characterize colloids recovered from experiments and field sampling studies.

C.E.A. Palmer, R.J. Silva, H.L. Hall, G.L. Klunder, R.E. Russo, and D.A. Wruck, LLNL: Direct Quantification of Organic Material in NTS Well Waters.

The goal of this research is to directly quantify total organic carbon content in NTS well waters, accounting for microbial growth after sample collection. An initial study has shown a marked sensitivity to apparent total organic carbon content to sample preservation methods used over time. These data are described below:

Well/Spring	Method A	Method B	Method C	Method D	Method E
4	0.2290	0.1130	0.0095	-0.0626*	0.0203
8	0.2470	0.5070	-0.0587*		-0.0154*
16D	0.2270	0.1350	0.0091	-0.0286*	0.0157
20W	0.2540	0.1530	-0.0213*	-0.0776*	0.0262
Cane Spring	0.5510	0.4160	0.2540	0.233	0.2680

*Negative number indicates inability to estimate zero-time concentration.

Method A: H₃PO₄, light, ambient temperature, plastic bottle

B: H₂SO₄, dark, cold room, plastic bottle

C: H₂SO₄, dark, cold room, glass bottle, (EPA protocol)

D: H₂SO₄, light, ambient temperature, glass bottle

E: Na NO₃, H₂SO₄, dark, cold room, glass bottle, (Whitbeck protocol)

The results show that total organic content can vary greatly depending on the preservation method and that in some instances it is difficult to extrapolate to a zero time total organic content as reflected by the negative values. A method is being developed for the more accurate measurement of low total organic carbon contents. This is accomplished by complexing carbon with Eu^{3+} , exciting the organic ligand with 354 nm laser light, and measuring organic carbon content by charge transfer and Eu fluorescence. Preliminary results are promising that this technique will yield better total organic carbon estimates independent of sample preservation method.

Summary of Important Comments Made During the Panel Discussion: (Panel Members: Mike Whitbeck, Brian Viani, Cindy Palmer, Jerry Kerrisk, Greg Choppin)

- Brian Viani:** Present studies overestimate colloid concentrations because of contamination and artifacts.
- Jerry Kerrisk, Greg Choppin, Mike Whitbeck:** Sampling disturbs a flow system; therefore we must determine how best to sample groundwater.
- Question by Bill Steinkampf:** Are the organics in J-13 water coating colloids or are they separate phases? **Answer, Mike Whitbeck:** At this point it is unknown whether the organics are coatings or not, or whether they are naturally occurring or oil introduced during drilling.
- Jae-il Kim:** Sampling water changes its partial pressure of CO_2 . This may induce colloid formation as an artifact by changing water chemistry.
- Arend Meyer:** You need to know the well construction techniques before sampling colloids in order to sort out potential contamination.
- Question posed by Ardyth Simmons to the panel:** What is the colloid concentration in J-13? Consensus was reached that we do not know the answer to this question. A strong interest was expressed in resampling well J-13 in order to confirm or deny earlier analyses. Jim Hunt recommended sampling under non-steady-state conditions; seismic events and rapid recharge events will increase turbidity and release of particles. Peter Vilks recommended sampling at different time intervals to ascertain the consistency of information.

TUESDAY MORNING, MAY 4, 1993

This session was intended to address the question: *1) Does the evidence support the likelihood for significant transport of radionuclides by colloids at Yucca Mountain?* On the basis of the presentations and subsequent panel discussion, it is uncertain whether the present state of knowledge allows a confident response to this question.

Before the scheduled program began, Linda Stetzenbach of UNLV gave a brief presentation regarding sampling of microbes in Nevada Test Site well and spring waters. She has determined that bacteria may survive in groundwaters despite the low nutrient environment. However, these microbes are difficult to culture using conventional agar. She has developed a low-nutrient growth medium, R2, which has been somewhat successful for culturing microbes from groundwaters. Gas chromatography of the organisms gives an

analysis of fatty acids that are genus/species specific, allowing correlations with known organisms provided their fatty acid structure is recorded in a database. Unfortunately, fatty acids from many microbes are not in existing databases. J-13 water contains on the order of 20-50 organisms/ml whereas springs often contain thousands of organisms/ml. Future plans are to test whether unique populations exist in particular aquifers or horizons within aquifers.

J.R. Hunt, UC: Radionuclide Migration at the Nevada Test Site.

This presentation described the result of two underground nuclear tests, one of which (Cheshire site) showed evidence of radionuclide migration in the groundwater, while the other (Cambric site) did not. Both tests have implications for radionuclide migration assisted by colloids. A number of problems are associated with the studies described. These include the pumping of samples which may artificially change the concentration of colloids, sample storage which may also affect apparent colloid counts, dynamic ultrafiltration, and colloids introduced as artifacts from the well casing.

The Cambric 3/4 kiloton event in 1965 was detonated in the water table at 300 m. Beginning in 1975, the monitor well located at the same depth 91 m from the blast was pumped for two years without any breakthrough of tritium observed. Two years later, the pump rate was increased and no breakthrough was observed until 1980-81. No radionuclides with known retardation factors greater than 6-10 were ever observed.

The Cheshire site was a larger blast detonated in 1975 at 1200 m depth. Waters pumped from a drillback into the blast cavity in 1983 yielded particle concentrations of 55 mg/l in the 200-6 nm size range and 10 mg/l in the 50-3 nm fraction, whereas formation waters in the 50-3 nm size range contained 4 mg/l colloids. Eu and Co were observed to be strongly partitioned onto colloids (<2% remaining in solution), and tended to remain in the cavity rather than migrating into formation waters. A satellite well drilled and sampled at approximately 200 m distance indicated that ^3H , ^{125}Sb and ^{137}Cs had migrated in the groundwater, although both Sb and Cs showed significant reductions in concentration relative to cavity waters or formation waters sampled near the cavity. This was especially true for Cs which showed a reduction of 3 orders of magnitude in concentration. Additionally, Cs and Na showed evidence of having participated in ion-exchange reactions which retarded their mobility.

This presentation also described particle flow experiments relative to colloid transport. Two processes may result in the clogging of fractures, weathering and secondary mineral formation, and attachment of colloids to fracture walls, thereby impeding colloid mobility. This produces a fracture in which there is darcy flow in the porous deposit on the fracture wall and open flow in the remainder of the fracture. Under a constant pressure gradient, particles move faster than water if excluded from the porous region, and the breakthrough curves for particulates will occur earlier than conservative molecular tracers although they will be more spread out. Experimental results show that small degrees of fracture clogging correspond to significant increases in head loss. Therefore, clogging of fractures is expected in natural systems, and colloid transport should be insignificant.

W.L. Polzer and E.H. Essington, LANL: Characteristics and Mobility of Actinides in an Aquifer in a Semi-Arid Region.

Liquid actinide-bearing waste at LANL is treated with iron sulfide and lime which removes most radionuclides by precipitation of iron hydroxide and calcium carbonate. However, when it is discharged at Mortendad Canyon actinide species remain in solution in very dilute concentrations which subsequently move up to 3400 m by porous flow in the subsurface. Four wells are employed to monitor groundwater flow in the shallow alluvial aquifer that lines the base of Mortendad Canyon. Actinides are characterized in terms of their concentrations, distribution ratios, oxidation states, ion-exchange properties, size fraction (colloids), chemical reactivity, and rate of movement. Effluent discharge averages about $40 \times 10^3 \text{ m}^3$ in the aquifer which has a storage capacity of $20\text{-}30 \times 10^3 \text{ m}^3$. Annual storm runoff ranges from $25\text{-}125 \times 10^3 \text{ m}^3/\text{yr}$. Before sampling, water is pumped for 30 minutes. Water chemistry ranged from pH 6.4 to 10.1, Eh > 200 mV and $\text{O}_2 > 0.3 \text{ } \mu\text{g/l}$. Sampled water was filtered to exclude particles greater than $0.45 \text{ } \mu\text{m}$.

Pu is reduced (III, IV) and was observed to decrease in concentration downslope from about 2×10^1 to $1 \times 10^3 \text{ mBq/l}$. Americium concentrations, however remained essentially constant to slightly increasing at about $2 \times 10^1 \text{ mBq/l}$. This results in nearly constant apparent retardation factors on the order of $1\text{-}4 \times 10^4$ for Pu, but systematically decreasing K_d 's for Am from 9×10^3 at the injection point to about 70-80 at the furthest well. In the wells and at waste outfall, Pu species are dominantly neutral, whereas Am species range from dominantly neutral to subequal neutral and anionic. Isotopic tracers added to the waste show that marked isotopic disequilibrium is maintained between the tracer and effluent actinides. This indicates that sorption of radionuclides onto groundwater colloids may have an element of irreversibility. Pu transport rates are 5-20 times slower than the conservative tracer ^3H , showing potential for retardation by colloids, rather than faster transport.

P. Vilks, J. Cramer, and D. Bachinski, AECL Res.: Colloid Natural Analog Studies at Cigar Lake.

The Cigar Lake U-deposit is in some respects a natural analog for the near-field environment of a nuclear waste repository in a saturated environment. The deposit contains 12% U as uraninite surrounded by clay in a sandstone aquifer. Groundwater flow has been observed to be from the south to north, and this system may provide a valuable test for radionuclide migration by colloids. The objective of the study was to determine particle concentrations, size distributions, compositions, radionuclide sorption on particles, particle generation, and geochemical evidence of actinide transport by radiocolloids.

Six boreholes in the vicinity of the deposit show dominant particle size distributions of about 0.5-1.25 mg/l in the 100-400 nm fraction and between 0.25 and 0.5 mg/l total concentration. In spite of dominant size fractions, surface area distributions are dominated by smaller particles because their surface area is so much larger.

Particle concentrations are observed to vary by as much as a factor of ten in any given well depending on when the water is sampled. Initial colloid concentrations systematically decrease during a given pumping cycle, eventually reaching a steady state. Once a new pumping cycle is initiated, another increase in colloid levels is observed. Changing the piezometer or purging the well with or without N₂ also affects colloid counts. This makes it difficult to interpret what the ambient colloid concentration is, and illustrates that apparent concentrations are very sensitive to sampling techniques. In spite of this, colloid counts are sensitive to and tend to reflect fracture mineralogy of the host rock including illite, chlorite, kaolinite, quartz, and feldspars. Alumina is generally restricted to clay particles > 0.45 µm. Fe-oxide is also generally restricted to larger particles, whereas carbonate and organic particles constitute a large fraction of the smaller colloids.

²³⁴U/²³⁸U activity ratios in the host rock are in equilibrium to slightly depleted in ²³⁴U (0.8 - 1), although the same ratios in both the groundwater and on the particulates is about 2. This indicates that the U in the colloids has been sorbed from the groundwater. A similar relationship is observed for ²²⁶Ra/²³⁰Th ratios. If all the ²³⁰Th in the colloids were to result from the ingrowth of ²³⁴U, then an maximum age of 8 ka can be assigned to them. Field derived K_d's exhibit a range over several orders of magnitude (U=2 x 10³-2 x 10⁷, Th=3 x 10³-9 x 10⁵, Ra=2 x 10³-1 x 10⁶) and average U concentrations in particles ranges from about 100-600 ppm.

The primary conclusions of this study indicate an element of irreversibility in the sorption of radionuclides on colloids implying that an understanding of colloid behavior is important in characterizing potential radionuclide migration. However, to this point there has been no significant transport of radionuclides from the ore body, through the clay layer, and into the surrounding sandstone aquifer.

P. Vilks and D. Bachinski, AECL Res.: Review of AECL Colloid Transport Experiments.

The objectives of these studies are to determine the mobility of colloid-sized and other suspended particles in fractures, and their role in radionuclide migration. Two approaches were taken in this effort. The first involved the evaluation of particle generation from fracture surfaces during groundwater flow. The second involved the characterization of filtration and remobilization of particles introduced into fractures using latex spheres, silica, clay and natural colloids. In this second effort the effect of water velocity, particle size, channeling, and fracture orientation were considered. Experiments were conducted on a quarried granite block 83 x 90 x 60 cm, with the flow field determined by 9 boreholes. Thus, it was possible to achieve a level of control over particle migration that cannot be achieved in the field.

After characterizing the hydraulic characteristics of the block, natural particle release was analyzed by flushing the block with colloid-free water followed by migration tests with non-sorbing tracers (uranine and bromine) and synthetic particles. Particle counts were determined by and Ultrafine Particle Size Analyzer (UPA) (6 nm to 2.5 µm) and a CLIMET

particle counter (0.4 to 100 μm).

Natural particles released from the block at a flow rate of 4-400 ml/h included quartz, clay, feldspar, calcite, and bacteria. The water used was a Na-Cl-HCO₃-SO₄ water with an ionic strength of 0.013. Particles as large as 40 μm were mobilized during the experiment and increasing the flow rate to the maximum increased the release of 5 μm particles and larger but did not affect the release of smaller particles.

In artificial colloid experiments, 72 nm latex breaks through at the same time as the tracer in experiments conducted at high flow rates, but breaks through slightly ahead of the tracer at lower flow rates. About 35% recovery was achieved during the tests, but all latex spheres were recovered by back flushing, indicating that the spheres had become lodged in the fractures along the flowpath during the experiment. Experiments conducted with 39 nm spheres clearly indicated a more narrow breakthrough curve and substantially less recovery for slow (1 ml/h) versus fast (400 ml/h) flow rates. For mixed 1-4 μm latex experiments, the spheres all appear in breakout curves after the tracer at low flow rates, with successively impeded recovery with larger size fraction. In one experiment, mixed coagulated latex spheres with two size ranges of 20-40 μm and 20-70 μm allowed the comparison of breakout curves for particles with a large, continuous size range. In this instance, the 20-40 μm flocs preceded the bromide tracer, with the 20-70 μm floc breakthrough at about 2-2.5 times the eluted volume of the smaller flocs and tracer, respectively. AECL plans future field-scale experiments using latex spheres and silica particles.

Comment by Don Langmuir: Field-scale experiments cannot be conducted at realistic flow rates, bringing into question the utility of the results.

T. Payne, ANSTO: Colloid Distribution at the Koongarra Uranium Deposit.

The Koongarra deposit is located in a flat region of seasonal monsoon storms, and consequently the groundwater level is shallow and the weathering profile is quite thick (hundreds of meters). A downward moving (15-30 m/Ma) weathering front has intersected the primary ore zone of the Koongarra uranium deposit, creating a dispersion fan which is elongate downstream in the direction of groundwater flow. Thus, the Koongarra deposit can be thought of as an analog to a waste repository because waste has been redistributed by groundwater into a fan which has extended 200 m over the last 1.5 Ma. As a consequence of these properties, the Alligator Rivers Analog Project (ARAP) was initiated with participation from ANSTO (Australia), JAERI (Japan), PNC (Japan), SKI (Sweden), UKDoE (U.K.), and USNRC (U.S.A.) from 1987-1993.

The groundwater at the site is a neutral Mg²⁺ bicarbonate water that has a neutral pH, slightly oxidizing Eh, and low total organic carbon. In many respects the water chemistry is quite similar to Yucca Mountain water although Na⁺ is the dominant cation at Yucca Mountain. U is elevated in the groundwater, ranging from several hundred ppb near the orebody to less than 1 ppb at a distance of 400 m. The ARAP strategy with respect to colloids was to sample them, determine their physical and chemical characteristics, measure

the size distributions--especially those bearing U and Th, and evaluate their ability to transport radionuclides. In applying the results of the ARAP project to Yucca Mountain it is important to answer whether colloids have facilitated radionuclides at Koongarra, to what extent the results are transferable, and whether Koongarra is a worst case scenario.

In order to avoid sampling problems, colloids were separated in the field by ultrafiltration in an N_2/CO_2 atmosphere at the well head. The samples remained sealed until they were analyzed. The filters were analyzed by SEM to determine the quality of filtration. The colloids were analyzed by SEM-EDS to qualitatively determine their composition. Although colloids in groundwaters surrounding the Koongarra deposit include U-Fe and uranyl silicate particles, kaolinite, chlorite-like particles, and mica-like particles, the structurally U-bearing colloids seem to be limited to the immediate vicinity of the weathered portion of the U-deposit. At Koongarra, colloid type also seems related to the mineralogy of the country rock. Studies of the colloids indicate that U migrates dominantly as a dissolved species. Th and Ac are chiefly associated with larger ($>1 \mu m$) particles. Colloids are present in low abundances and may carry measurable Th, U, Ac, and Fe. In $1 \mu m$ -filtered groundwater, 5-82% of ^{230}Th and 0.1-2.5% of ^{238}U is partitioned onto colloids. In the case of Th, however, this represents a large fraction of an element that is extremely insoluble. Although colloid transport is of greatest importance for Ac and Th, colloids have been rather unimportant in transporting radionuclides at Koongarra.

Summary of Important Comments Made During the Panel Discussion: (Panel Members: Jim Hunt, Peter Vilks, Wilfred Polzer, Tim Payne)

•Question from Bruce Robinson to the panel: What is to be gained from experiments with synthetic colloids considering those experiments perturb the natural flow field? Answer, Peter Vilks: Information regarding size effects can be gained. Answer, Jim Hunt: Forced-flow experiments do not mimic reality. Nature operates under constant head. These conditions result in filtration of the colloids.

•Question from Julie Canepa to the panel: What does the project stand to learn from natural analogs? Answer, Wilfred Polzer: Irreversibility and ion exchange are realities in colloid-mediated radionuclide migration. Answer, Jim Hunt: The Nevada Test Site is a "pseudo" natural analog that shows strong retardation of radionuclide migration. A small amount of trapped colloid produces a big increase in fracture flow resistance. (It was noted that no radionuclide migration testing has been conducted for the vadose zone such that no inferences can be drawn about undersaturated flow)

•Question from Ines Triay to the panel: What field experiments should be conducted at Yucca Mountain? Answer, Bruce Robinson: Colloid tracer studies conducted with dissolved conservative tracers. Answer, Peter Vilks: Before conducting field experiments, a sound understanding of the flow system is needed.

TUESDAY AFTERNOON, MAY 4, 1993

This session was intended to address the question: 1) Can we bound the total mass of colloidal material that may be present in the repository environment? 2) Can we bound the relative contributions to the total colloidal mass from major sources? On the basis of the presentations and subsequent panel discussion, it is uncertain whether the present state of knowledge allows a confident response to these questions. An observation of some interest is that alteration of the waste form itself may be a source of colloids that may have to be considered.

Before the scheduled program began, Peter Kearn of ORNL gave a brief discussion regarding optical monitoring of suspended particles ($>1\mu\text{m}$) in boreholes. He noted that no matter how gently the device was lowered into the water, an increase in the number of particles was observed. He concluded that any perturbation, such as the onset of pumping, will disturb the initial colloid concentration. His experience suggests letting the system come to a steady state before pumping at 100-500 ml/min.

D. Morris, LANL: Formation and Physico-Chemical Properties of Radiocolloids.

For the purposes of this report, radiocolloids were defined as being composed entirely of hydrolyzed radionuclides with no sorbing substrate involved. The radiocolloid formation process involves hydrolysis of the cations, condensation of the hydroxyl groups, and oligomerization of condensed hydroxyl groups. In order for radionuclides to represent a problem for waste isolation via colloid migration, the candidate radionuclide must be in the waste package inventory in sufficient concentration and have a high charge/radius ratio. These criteria group radionuclides in to four categories, of decreasing importance, with respect to radiocolloid formation: 1) Pu, 2) Am, Th, Pa, 3) U, Np, Ac, Pb, Sn, and 4) Ra, Ni, Sr.

This study is similar to other radionuclide speciation studies except it considers transport potential and reactivity of the radionuclide complexes. This approach is of added importance since radiocolloids are metastable, making thermodynamic modeling impossible. The chemical properties to be characterized include synthesis conditions, stoichiometry, and reactive trends, whereas physical properties include particle size, density, and charge. In the past, a number of methods have been used to synthesize Pu radiocolloids, however, none involves a process likely to be repeated in nature. In general, oversaturated solutions age to form colloids whereas undersaturated solutions do not. Radiocolloids tend to increase in size with time to range in size from 3 nm to 350 nm although the larger size is rare. Small radiocolloids (2 nm) have a density of 9 g/cm^3 compared to 11 g/cm^3 for PuO_2 , and tend to form elongate cylinders.

The properties of Pu radiocolloids formed in UE-25 p#1 water at 25 and 60°C and pH between 6 and 8.5 indicate that the structure is similar to PuO_2 as determined by x-ray diffraction, infrared spectrometry, raman spectroscopy, etc. In general Pu colloids form under a variety of conditions, but do not form from undersaturated solutions. However, these Pu radiocolloids are unstable with respect to precipitation at $\text{pH}>5$. Radiocolloids may also participate in a variety of reactions. Some important questions to address include whether

radiocolloids are a near-field issue, or whether they may act as a secondary source term for dissolved species in the far field.

J.C. Bates, and E.C. Buck, ANL: Colloids From Waste-Form Reactions.

Experiments were conducted to evaluate the formation of colloids from glass, UO_2 , and spent-fuel waste. The approach was designed to study waste-form degradation under conditions likely to be encountered in the near field. At present it is not possible to study the interaction of the waste form and waste package since no firm decisions have been made regarding the materials to be used in the latter. However, if the degradation of the waste package acts to retard colloid formation or migration, the present studies may provide conservative data.

Hot drip tests have been performed to simulate expected conditions in an unsaturated repository. Water passed across the waste form was collected, separated, and analyzed for colloid content. Colloids may form by a variety of processes including: 1) spallation products from the waste form, 2) radionuclides released directly into solution where they may subsequently form radiocolloids or pseudocolloids, 3) or precipitation from solution into radionuclide-bearing smectite clays.

The surface of glass develops an alteration rind with secondary phases on the surface as it reacts with water vapor. As alteration proceeds, brockite crystallizes in the rind and the actinides are mobilized and concentrated into discrete phases. Also, glasses of different composition do not behave similarly during alteration. Water dripped onto the surface of the glass results in spallation of the alteration rind, increasing the release rate. Smectite has been observed to precipitate onto the surface of the newly exposed glass. Colloids separated from these experiments include 50-100 nm birnessite and smectite as well as an U-Ti-O phase. Other colloidal phases identified include heulandite and mica.

Water dripped onto UO_2 pellets reacts to form $U_3O_8 \cdot 8H_2O$. This results in the release of U and the formation of secondary phases. Unlike the glass experiments which showed fairly constant radionuclide release rates, pellet experiments tend to show that after an initial period of little release, rapid release followed until a distinct break is observed signaling a significant reduction in release. For drip tests conducted with actinide saturated solutions, the release of Am was shown to be greatly reduced. The initial release pulse is related to etching of grain boundaries which may ultimately result in their spallation. Schoepite, a U-Ca-Na hydrate phase, was also observed.

W.J. Gray, PNL: Colloid Formation From Spent Fuel Dissolution.

This report summarizes two series of experiments conducted on spent fuel and J-13 water, the first conducted in fused silica vessels at 25°C and the second in stainless steel vessels at 25 and 85°C. Water was periodically sampled, filtered and analyzed to evaluate radionuclide release. Ultrafiltration reduced the activity of $^{239+240}Pu$ in solution by up to an

order of magnitude, indicating that some radionuclides were present in the water as colloids. ^{241}Am and ^{244}Cm concentrations were often reduced by two orders of magnitude or more by filtration, indicating an even stronger component of colloids in the water. Filtration produced only a small reduction in ^{237}Np .

In summary, 20-60% of Pu and >90% of Am and Cm was present in colloidal material. U and Np were not transported by colloids in significant quantities. Radionuclide release from the waste form was not enhanced at 85°C relative to ambient temperature experiments. Annual release rates estimated from these tests, as a fraction of 1000-year inventories is expected to be 3-4 orders of magnitude (10^{-8} - 10^{-9} vs 10^{-5}) below NRC standards.

Annemarie Meike, LLNL: Colloid Formation From Spent Fuel Dissolution.

This report summarized no data, rather listed issues related to anthropogenic activity in Exploratory Studies Facility or repository construction and how they may introduce colloids into the waste isolation system. Construction requires the use of materials such as shotcrete, diesel, resin, bentonite, waste package material, etc. that may contribute to the colloid budget at Yucca Mountain. The effect of these materials and construction activity should be considered.

M. Gardiner, AEA Tech., U.K., gave a brief presentation the next day regarding colloids produced in cementitious environments, showing that 10^7 particles/l (<1mg/l) of hydrous calcium silicates may be expected.

Schön Levy, LANL: Gels and Colloids Around Yucca Mountain.

Past hydrothermal activity in the Topopah Spring Member may provide important information regarding the formation and dispersion of colloids as a natural analog in the repository horizon. During cooling of the ash-flow sheet after emplacement, the Topopah tuff cooled, probably in unsaturated conditions, through a temperature interval similar to the near-field environment induced by a repository. This produced an orange altered horizon at the top of the impermeable basal vitrophyre which may have caused local perching of water. Alteration in this horizon is controlled by the down-flow of water in existing fractures.

Deposition in fracture fillings and dissolved shards shows horizontal layering that is interpreted to represent "sedimentation" of colloidal material to form fracture and void filling gels. These subsequently crystallized to an assemblage dominantly composed of amorphous silica, heulandite and clinoptilolite, and Fe- and Mn-oxide/hydroxide. Other gel crystallization products include smectite, saponite and Cu- and Fe-sulfates and cristobalite. Thus, the life history of a colloid includes generation, transportation, deposition, and crystallization.

In the bedded tuffs of the Calico Hills, large pore spaces also appear to be filled with colloidal material that later crystallized from the edges inward into silica and zeolite. A similar situation is also found within the bedded tuffs below the basal vitrophyre of the

Topopah Spring Member.

In conclusion, it appears that such moderately to nonwelded tuffs acted as a sink for colloids and may be expected to do so in the future. Alteration and colloid generation occurs under locally saturated, but globally undersaturated conditions. In addition, the composition of the colloidal accumulation varies as reflected in the mineral chemistry and assemblage of crystallized gels. Some important issues are raised by this study. For example, what fraction of the paleo-colloid budget is represented by the accumulations? There is also considerable lateral variation in the degree of alteration in some horizons, making it difficult to determine what is representative. It is also unknown how the water budget in the paleohydrologic system would correspond to the near-field environment. Finally, would the colloids accumulate and crystallize before or after radionuclide release?

Summary of Important Comments Made During the Panel Discussion: (Panel Members: Heino Nitsche, Bob Silva, John Bates, Walt Gray, Schön Levy)

- Bob Silva: Natural analogs may not be important. Back fill of the waste form will produce colloids that would not occur otherwise. Colloid migration in the near field is more important than in the far field.
- Heino Nitsche: We need to understand the effects of human intrusion and man-made materials, and the mechanisms of colloid transport before we can assess the importance of colloids. Response by Julie Canepa: It should be remembered that the list of materials that will be used in the Exploratory Studies Facility will not all be used in, or remain underground. For example, much of the water will be used outside for dust suppression.
- John Bates: We cannot do the proper tests on radionuclide release from the waste form/package until a definitive suite of packaging materials is chosen. Until then, it will be difficult to estimate a source term.

WEDNESDAY MORNING, MAY 5, 1993

This session was intended to address the questions: 1) To what extent are experiments conducted in other media pertinent to Yucca Mountain? 2) Can the physico-chemical behavior of colloids be predicted from laboratory data? 3) What are the most critical experiments needed to address the issue of colloid transport at Yucca Mountain? It appears that other experiments are of some use to the Yucca Mountain Project. Naturally, any insight into colloid behavior is pertinent. The physico-chemical characterization of colloids will have to rely on laboratory data, especially in areas where experimental studies are a sole data source. It appears that combined lab and field experiments will be needed to address these issues, especially those conducted in fractured media and at high temperature.

I. Triay, LANL: Review of LANL Colloid Investigations.

Experiments at LANL have dealt with the formation of hydrolyzed Pu radiocolloids from solutions containing Pu⁴⁺ and Pu⁶⁺ in J-13 water interacting with pure minerals and crushed tuff. Most colloids are on the order of a few nm in size, but the addition of bicarbonate results in colloids hundreds of nm in diameter. The solutions can be analyzed with light scattering techniques to obtain diffusion coefficients and size distributions.

Two types of experiments have been conducted. The activity of solutions from batch sorption experiments was counted before and after in order to obtain an apparent K_d between liquid and solid phases. The solid material was immersed in pure water afterward in order to evaluate desorption. In general there is reasonable agreement between experiments, both sorption and desorption, and Pu⁴⁺ and Pu⁶⁺ solutions. Apparent K_d 's are on the order of 10^4 .

Dynamic transport experiments through crushed tuff showed variable results. Pu⁴⁺ is largely retained by tuff, but a 2% (Pu concentration in eluted solution is 2% of the original concentration) breakthrough is observed to appear ahead of tritiated water, a conservative tracer. Pu⁵⁺ and Pu⁶⁺ elute at 30-70% of their original concentrations, in strong disagreement with the batch experiments. It is believed that Pu⁵⁺ is not a strongly sorbing oxidation state. Column experiments for pure mineral sorption also do not give the same K_d 's as batch experiments. A few percent breakthrough ahead of tritiated water was also observed for colloids formed from Pu⁴⁺. It is believed that kinetic effects are responsible for the difference between batch experiments and the column experiments. Column experiments were performed over a shorter time-scale in which sorbing species may not have had time to form.

Other experiments have been performed related to stability of colloids and the effect of organic coatings. In the case of the latter, organic coatings have been observed to both enhance and retard sorption.

J. McCarthy, ORNL: Colloid Transport Field Experiments.

The experiments reviewed were conducted in a shallow sandy aquifer with all the usual characteristics of natural groundwater systems including slow flow and heterogeneity in the porosity and chemistry of the system. This enables a determination of how well laboratory experiments may be expected to scale to the field.

Transmissivity vectors were determined between a number of wells in a 5 x 5 m field. Subsequently, a two-well injection-collection forced flow system was imposed, although numerous wells were monitored. The tests were conducted with water (natural pond water) rich in organic matter (30 ppm) and Fe-OH complexes, thus allowing determination of the effects of these materials on colloid transport. The mass of the organic macromolecules in the injection solution ranged from 3-100 μ MW. The organic matter is present as both solutes and macromolecules, and physical characterization of organic colloid transport requires knowledge of size, charge, hydrophobicity, adsorption, binding of contaminants, changes in properties of the flowpath, etc.

The results of combined field and lab tests showed broad breakthrough curves with

extensive tailing for organic matter and some retention in the matrix. Larger organic molecules were preferentially retarded over smaller ones. It appears that organic matter maintains a negative charge on Fe-OH colloids as well as enhancing the breakthrough and the fraction of other colloids transported. For example, in field tests Br^- tracer breaks through ahead of Fe-colloids although the breakthrough is more than expected.

J. Wan, NM Tech.: Colloid Transport in Unsaturated Media.

These experiments were conducted in glass webbing with a microscopic structure of small interconnected channels. The medium was partially saturated such that there were three distinct phases, solid, liquid, and dispersed gas bubbles producing two important interfaces, gas-water and solid-water. Hydrophobic and hydrophilic colloids were introduced as clay particles, bacteria, and latex spheres. Forced flow was imposed and the collection of particles at interfaces and their transport through the medium was observed.

Hydrophobic particles collect at both gas-water and solid-water interfaces, whereas hydrophilic particles collect primarily at gas-water interfaces. Collection at solid-water interfaces appears to be reversible and gas-water interfaces appear to be the locus of irreversible aggregations of particles.

Column experiments using silica sand as a solid medium gave fairly narrow breakthrough curves for hydrophilic particles, although the particle concentration in the eluted solution decreased with decreasing saturation. Hydrophobic particles, on the other hand, show broad breakthrough curves also with greater retardation at smaller degrees of saturation.

In conclusion, retardation in unsaturated media is proportional to the degree of saturation because of particle retention at the gas-water interface. Sorption depends on the degree of hydrophobicity, thereby variably partitioning particles between the two interfaces.

Question by Julie Canepa: How would gas-water interfaces move in nature?

Answer: The experiments were intended to mimic natural effects such as increased rainfall or aridification.

J.H. Wolfram, INEL, and J.W. Costerton, MSU-ERC: Microbial Mobility and Metal Uptake Phenomena.

Microorganisms in the subsurface are generally 1-2 μm in size, come in a variety of shapes, and have the ability to metabolize a variety of compounds including CO_2 , CH_4 , CH_3OH , proteins, resins, pesticides, etc. They also may survive in extreme conditions including heat, pressure, radiation, salinity, and a wide range of pH. Microbes have recently been recovered deep within the vadose zone and in deep groundwaters. Bacteria found in such nutrient-starved environments may become dormant and difficult to detect, decreasing in size to about 0.3 μm . In addition, many microorganism concentrate heavy metals in their bodies up to 1000 ppm. Based on these observations, the potential exists for bacteria to

transport radionuclides in the subsurface.

R. Rundberg, LANL: NAGRA and SKB: Review of Colloid Research Programs.

The Swiss logic diagram for colloid investigations was presented, and based upon that logic they have determined that colloids are not a significant problem in granitic repositories. A review of natural colloid concentrations measured by the Swiss and U.S. programs was reviewed. Of particular interest is the ubiquitous potential for artifact colloid generation due to changes in water chemistry imposed by sampling. Increasing Ca^{2+} concentration may decrease colloid abundances. This may be due to increased sorption of colloids onto wall rock by decreasing the thickness of the double layer surrounding the colloid.

NAGRA studies appear to have determined that natural colloid abundances are low, that colloids are unstable, and that sorption of radionuclides onto colloids is not sufficient to compete with the surrounding rock matrix. These studies may be pertinent to Yucca Mountain in that they emphasize the need for careful sampling techniques, the groundwaters studied have a similar chemistry, major rock forming minerals are somewhat similar, and the natural colloid abundances may be about the same as in J-13 water.

The SKB program has emphasized the field measurement of colloid transport, the transport of Fe-oxides in quartz columns, and the uptake of radionuclides by bacteria. This program may have some relevance to Yucca Mountain because of the generic nature of the studies.

Summary of Important Comments Made During the Panel Discussion: (Panel Members: Robert Rundberg, John McCarthy, Peter Vilks, Mike Gardiner, Mike Whitbeck, Paul Reimus)

- Arend Meijer: Pursuing natural analogs may be interesting work, but it is difficult to see how such studies will give clear direction to Performance Assessment.
- Mike Gardiner: Lab experiments scale well to the field, but neither reflect reality in nature. A predictive model is needed for nature in order to use lab and field data.
- Paul Reimus: Different mechanisms may be operating in the lab and in the field. For example, surface forces, grain size differences, and hydrodynamics may all be different. In general, experiments need to be designed to test which criteria are important in colloid transport.
- John McCarthy: Some aspects of colloid transport are understood. Others are not such as the stability of colloids at elevated temperature and transport in the vadose zone.
- Paul Reimus: It would be advisable to piggyback testing onto other experiments that have been planned.
- Peter Vilks: It may be advisable to use silica or clay as colloids in experiments. These would behave most like groundwater colloid already present.
- Mike Gardiner: Organic colloids could be labeled with ^{14}C . For inorganic colloids it may be necessary to use them in high concentration to see beyond the background colloid

concentration.

•Don Langmuir and Ginny Colton-Bradley: High-temperature experiments under unsaturated conditions with and without waste form present should allow assessment of colloid stability, transport, etc. in the near field.

WEDNESDAY AFTERNOON, MAY 5, 1993

J.I. Kim, TUM: Observations and Conclusions Relevant to Colloid Transport at Yucca Mountain.

A main objective and challenge to colloid studies is how to adequately localize and analyze mobile particles in a representative fashion. Dissolved radionuclides may disperse in the geologic barrier in a predictable fashion analogous to a chromatographic column. However, colloids have the potential to disrupt that dispersion by forming radiocolloids or by attachment to groundwater colloids.

The interaction of water with the waste form/package and Engineered Barrier System (EBS) may mobilize radionuclides. However remineralization in the near-field may itself form a new barrier. Subsequent interactions of dissolved radionuclides with the geologic and aquifer barriers may result in the generation of secondary and tertiary mobilization.

Experiments show that the loss of CO₂ can result in the formation of colloids. For example, Am-CO₂ aqueous complexes will dissociate to colloidal Am-OH complexes when CO₂ is lost. Subsequent analysis of filtrate in such a case will give incorrect information regarding the behavior of this element in solution. For pseudocolloids, Cm³⁺ concentrations in filtrates drop with increasing pH, indicating increased sorption on the colloid. Similar situations are found for Th⁴⁺ and Np⁵⁺. In many instances the apparent solubility of radionuclides depends on the smallest filter used. In general, it appears that organic and inorganic pseudocolloids can be mobile in groundwater. Radiocolloids probably are immobile as they and their hydrolyzed complexes will sorb to the rock matrix. Great care should be taken in the sampling and preservation of colloids and groundwater samples. Where possible, groundwater, colloids, and sediment should be sampled together with care taken to prevent a change in the partial pressure of dissolved gases. Water samples should be stored in a cold environment (10°C) to prevent bacterial growth.

The preceding talk was the final technical presentation of the workshop. Before proceeding with the final panel discussion, Ines Triay of LANL presented a preliminary strategy for dealing with the colloid issue, based in part on insight gained from the conference. The programmatic objective is to evaluate whether colloids will significantly increase radionuclide release to the accessible environment. It was noted that information is needed in the areas of: 1) colloid sampling techniques, 2) colloid generation, 3) colloid stability, 3) the sorption/desorption of radionuclides onto colloids, and 3) colloid transport. The accompanying logic diagram was presented, giving decision points for treatment of the

colloid issue by the Yucca Mountain Project.

Ardyth Simmons, DOE, then presented, for input by the attendees, a list of recommendations that would be made to DOE management. Clearly a better understanding of hydrologic parameters is needed, with emphasis on the unsaturated zone, and investigations should continue in this direction. Also information should be made available as soon as possible on waste package materials. A careful sampling of new wells is needed, as well as a resampling of well J-13 to confirm existing analyses. Mathematics for colloid modeling is in place, but what is needed prior to further refinement of the models is careful bounding experiments at all scales. Integration with the Nevada Test Site program could prove most beneficial, for well sampling and for a transport experiment on migration in the unsaturated zone. There may be additional tests planned within the YMP program upon which colloid sampling and testing for migration of colloids could be piggybacked. Furthermore, YMP needs to focus on parameters that are needed to be known with a high degree of accuracy, e.g., concentration, size, percent of organic coatings on particles, and adsorption/desorption parameters for colloids. The strategy outlined at this meeting appears reasonable for achieving goals toward understanding the significance of colloids at Yucca Mountain.

Summary of Important Comments Made During the Panel Discussion: (Panel Members: J.I. Kim, Ardyth Simmons, Julie Canepa, Bill Steinkampf, Brian Viani, Eric Nuttall, David Morris, Bruce Robinson)

- J.I. Kim: In addition to changes in the partial pressure of CO₂, growth of microorganisms can affect water samples by changing the pH.
- John McCarthy: Characterizing the large number and type of microorganisms is a complex problem.
- Paul Reimus: Polystyrene spheres chosen for C-well tests have surface properties similar to natural colloids.
- David Stahl: Some progress has been made in choosing candidate materials for the waste packages. At the present time several alloys are still under consideration including copper, high-Ni steel, stainless steel, and other Ti and Ni-bearing alloys.
- Jiamin Wan: The transport of water in the vadose zone must be understood in order to design experiments that mimic those conditions.
- Julie Canepa: A hot repository may exacerbate colloid formation from man-made materials as well as destroying near-field buffers.

Comments Related to the Yucca Mountain Project Strategy:

- Maury Morgenstein: The Project needs to prioritize experimental strategy so that, if possible, the issue of colloid transport can be put to rest. This may save a lot of unnecessary effort.
- Ines Triay: The position of testing strategies on the flow chart does not reflect a chronology. In other words, we will prioritize the testing program.
- Arend Meijer: The most important issue is whether colloids travel along fractures in the vadose zone.
- Stephen Nelson: If it can be demonstrated that colloids cannot migrate to the accessible environment in far field groundwater, doesn't that eliminate the need to consider all other issues in the flow chart? Response by Don Langmuir: That may seem to be the case, but

the regulatory community will not see it that way. They will probably focus on migration from the near field.

•Brian Viani: It may be important to understand the effects of man-made materials and activities on colloid formation. All waters sampled from project testing should be examined for colloids where practical.

Yucca Mountain Site Characterization Project Colloid Workshop
May 3-5, 1993
Santa Fe, New Mexico

Co-Chairs: Ines R. Triay, Los Alamos National Laboratory
Ardyth M. Simmons, Department of Energy, Yucca Mountain Project

Administrative Organizers: Alan J. Mitchell, Los Alamos National Laboratory
Ruth J. Sherman, Los Alamos Technical Associates

Host: Los Alamos National Laboratory

Objective: to evaluate whether colloids will significantly increase radionuclide release to the accessible environment at Yucca Mountain.

REGISTRATION:

Sunday May 2, 1993

5:00-7:00 PM

Refreshments will be served

Monday May 3, 1993

7:00-8:00 AM

PROGRAM:

Monday May 3, 1993

Morning Session: Colloid Transport Calculations

Moderator: Everett Springer, LANL

8:00-8:10	Welcome	Julie Canepa, LANL
8:10-8:30	Statement of Workshop Goal	Ardyth Simmons, DOE/YMP
8:30-9:00	Colloids: A Performance Assessment Perspective	Mike Wilson, SNL
9:00-9:30	Colloid Transport Calculations with CTCN	H. Eric Nuttall, UNM
9:30-10:00	Colloid Modeling Studies	Bill Lee, Environmental Evaluation Group
10:00-10:15	Break	
10:15-12:00	Panel Discussion Moderator: Everett Springer Panelists: Malcolm Siegel, Mike Wilson, Eric Nuttall, and Bill Lee	
	Question to be answered by the panel: Can we bound the potential significance of colloid transport at Yucca Mountain?	
12:00-1:00	Hosted Lunch	

ENCLOSURE 3



Monday May 3, 1993

Afternoon Session: Evidence of Colloids from Sampling Studies

Moderator: Bill Steinkampf, USGS

- | | | |
|-----------|---|------------------------------------|
| 1:00-1:30 | Humic Materials in Well J-13 Water | Greg Choppin, FSU |
| 1:30-2:00 | Suspended Solids in Well J-13 Water | Jerry Kerrisk, LANL |
| 2:00-2:30 | Colloids in Waters at the NTS and Vicinity | Michael Whitbeck, DRI |
| 2:30-3:00 | Characterization of Inorganic and Organic Colloids from the NTS | Brian Viani and Cindy Palmer, LLNL |
| 3:00-3:15 | Break | |
| 3:15-5:00 | Panel Discussion
Moderator: Bill Steinkampf
Panelists: Greg Choppin, Jerry Kerrisk, Michael Whitbeck, Brian Viani, and Cindy Palmer | |

Questions to be answered by the panel:

Do we have sufficient data to establish an upper limit on the amount of suspended solids in the groundwater at Yucca Mountain?

What is the most likely nature of the colloids in the groundwater at Yucca Mountain?

How should future colloid sampling studies be conducted?

Tuesday May 4, 1993

Morning Session: Evidence of Colloid Transport at the Field Scale

Moderator: Bruce Robinson, LANL

- | | | |
|-------------|--|--------------------------|
| 8:00-8:30 | Radionuclide Migration at the NTS | James Hunt, UC, Berkeley |
| 8:30-9:00 | Actinide Mobility Through an Aquifer in a Semi-Arid Region | Wilfred Polzer, LANL |
| 9:00-9:30 | Colloid Natural Analog Studies at Cigar Lake | Peter Vilks, AECL |
| 9:30-10:00 | Migration From a Transuranic Waste Disposal Site in the Vadose Zone | Jim Wolfram, INEL |
| 10:00-10:30 | Colloid Distribution at the Koongarra Uranium Deposit | Tim Payne, ANSTO |
| 10:30-10:45 | Break | |
| 10:45-12:00 | Panel Discussion
Moderator: Bruce Robinson
Panelists: Jim Hunt, Will Polzer, Peter Vilks, Tim Payne, and Jim Wolfram | |

Question to be answered by the panel:

Does the evidence support the likelihood for significant transport of radionuclides by colloids at Yucca Mountain?

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|------------|--------------|--|
| 12:00-1:00 | Hosted Lunch | |
|------------|--------------|--|

Tuesday May 4, 1993

Afternoon Session: Potential Sources of Colloids at Yucca Mountain

Moderator: David Morris, LANL

- | | | |
|-----------|--|-----------------------|
| 1:00-1:30 | Review of Formation of Radiocolloids | David Morris, LANL |
| 1:30-2:00 | Colloids from Waste Form Reactions | John Bates, ANL |
| 2:00-2:30 | Colloids from Spent Fuel Dissolution | Walt Gray, PNL |
| 2:30-2:45 | Other Introduced Materials: Considerations for Colloid Formation | Annemarie Meike, LLNL |
| 2:45-3:15 | Gels and Colloids around Yucca Mountain | Schon Levy, LANL |
| 3:15-3:30 | Break | |
| 3:30-5:00 | Panel Discussion
Moderator: David Morris
Panelists: Heino Nitsche Bob Silva, John Bates, Walt Gray, and Schon Levy | |

Questions to be answered by the panel:

Can we bound the total mass of colloidal material that may be present in the repository environment?

Can we bound the relative contributions to the total colloidal mass from major sources?

- 6:00- No host dinner at Rancho De Chimayo
Transportation provided - 6:00 PM departure time.

Wednesday May 5, 1993

Morning Session: Laboratory and Field Experiments Relevant to Yucca Mountain

Moderator: Arend Meijer, Jacobs Engineering

- | | | |
|-------------|--|-----------------------|
| 8:00-8:25 | Review of LANL Colloid Investigations | Ines Triay, LANL |
| 8:25-8:55 | Colloid Transport Field Experiments | John McCarthy, ORNL |
| 8:55-9:15 | Colloid Transport in Unsaturated Media | Jiamin Wan, NM Tech |
| 9:15-9:45 | Review of Colloid Transport Investigations in the NAGRA and SKB Programs | Robert Rundberg, LANL |
| 9:45-10:15 | Review of AECL Colloid Investigations | Peter Vilks, AECL |
| 10:15-10:30 | Break | |
| 10:30-12:00 | Panel Discussion
Moderator: Arend Meijer
Panelists: Paul Reimus, John McCarthy, Robert Rundberg, and Peter Vilks | |

Questions to be answered by the panel:

To what extent are experiments conducted in other media pertinent to Yucca Mountain?

Can the physico-chemical behavior of colloids be predicted from laboratory data?

What are the most critical experiments needed to address the issue of colloid transport at Yucca Mountain?

- 12:00-1:00 Hosted Lunch

Wednesday May 5, 1993

Afternoon Session: Future Direction of Colloid Studies in YMP

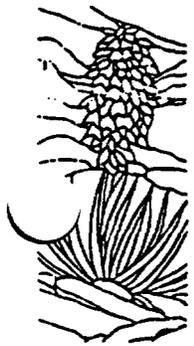
Moderator: Ines Triay, LANL

- | | | |
|------------------|--|--------------------------------|
| 1:00-1:45 | Observations and Conclusions Relevant to Colloid Transport at Yucca Mountain | J. I. Kim, TUM |
| 1:45-2:05 | Colloid Strategy for the Yucca Mountain Project | Ines Triay, LANL |
| 2:05-2:15 | Break | |
| 2:15-2:30 | Priorities to be Considered by the Panel | Ardyth Simmons, DOE/YMP |
| 2:30-4:50 | Panel Discussion
Moderator: Ines Triay
Panelists: J. I. Kim, Ardyth Simmons, Julie Canepa, Bill Steinkampf, Brian Viani, Malcolm Siegel, Eric Nuttall, David Morris, and Bruce Robinson | |

Question to be answered by the panel:

Relative to the objective of the workshop, what are the priorities for future colloid studies in the Yucca Mountain Project?

- | | | |
|------------------|------------------------|---------------------------|
| 4:50-5:00 | Closing Remarks | Julie Canepa, LANL |
| 5:00 | Adjourn | |



**Yucca Mountain Site Characterization Colloid Workshop
May 3-5, 1993
Santa Fe, New Mexico**

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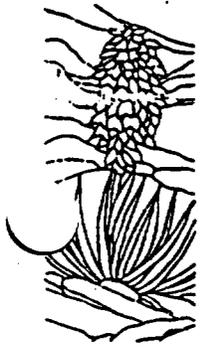
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ENCLOSURE 4





Yucca Mountain Site Characterization Colloquium Workshop
May 3-5, 1993
Santa Fe, New Mexico

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Yucca Mountain Site Characterization Colloid Workshop
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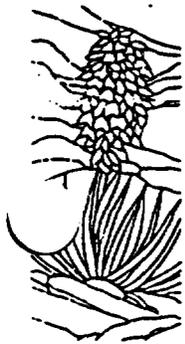
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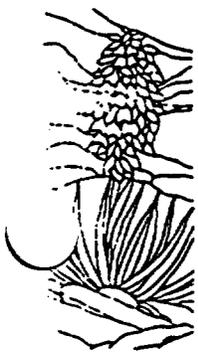
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May 3-5, 1993
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YUCCA MOUNTAIN
SITE CHARACTERIZATION
PROJECT

OPENING REMARKS AND
WORKSHOP GOALS

Presented by
LOS ALAMOS NATIONAL LABORATORY
DEPARTMENT OF ENERGY COLLOID WORKSHOP
SAN JUAN, NEW MEXICO



Approved by
ADAM SMITH
DEPARTMENT OF ENERGY

MAY 15, 1983

PURPOSE OF WORKSHOP

- **To address the issue of whether colloids will significantly increase radionuclide release to the accessible environment at Yucca Mountain**
- **If the answer to the question is “possibly” or “yes”, then to obtain guidance for colloid characterization**

QUESTIONS

In addressing the issue for Yucca Mountain, we will attempt to answer the following:

1) How can we bound the problem?

- Under what conditions will colloidal transport be significant?**
- Total mass of colloidal material that may be present in repository environment?**
- Relative contribution to total colloidal mass from major sources?**

2) What data are available?

- From sampling studies**
- Relevance of experiments conducted in other media**

QUESTIONS

(cont'd.)

- 3) What types of colloids exist at Yucca Mountain?**
 - **Upper limit on amount of suspended solids in groundwater at Yucca Mountain?**

- 4) How can we sample colloids?**
 - **How should future colloid sampling studies be conducted?**

- 5) How can we characterize colloidal transport at Yucca Mountain?**
 - **Will laboratory data predict the physico-chemical behavior of colloids?**
 - **What are the most critical experiments?**
 - **What are the priorities for future colloid studies?**

AGENDA

- **Colloid Transport Calculations**
 - **Use performance assessment and sensitivity studies to set framework**
- **Sampling Studies at NTS**
- **Evidence of Field-Scale Colloidal Transport**
- **Potential Sources of Colloids at Yucca Mountain**
- **Laboratory and Field Experiments Relevant to Yucca Mountain**
- **Future Direction of Studies**

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Eric Nuttall (UNM - consultant)

PROCESS

- **Conducted extensive literature survey**
- **Performed and will perform sensitivity studies in PA**
- **Developed draft strategy in keeping with SCP goals**
- **Draw on national and international experts for workshop**
- **Based on outcome of workshop, may revise strategy**
- **Will prepare report for management that evaluates significance of colloidal transport at Yucca Mountain**

Colloids:
A Performance-Assessment Perspective

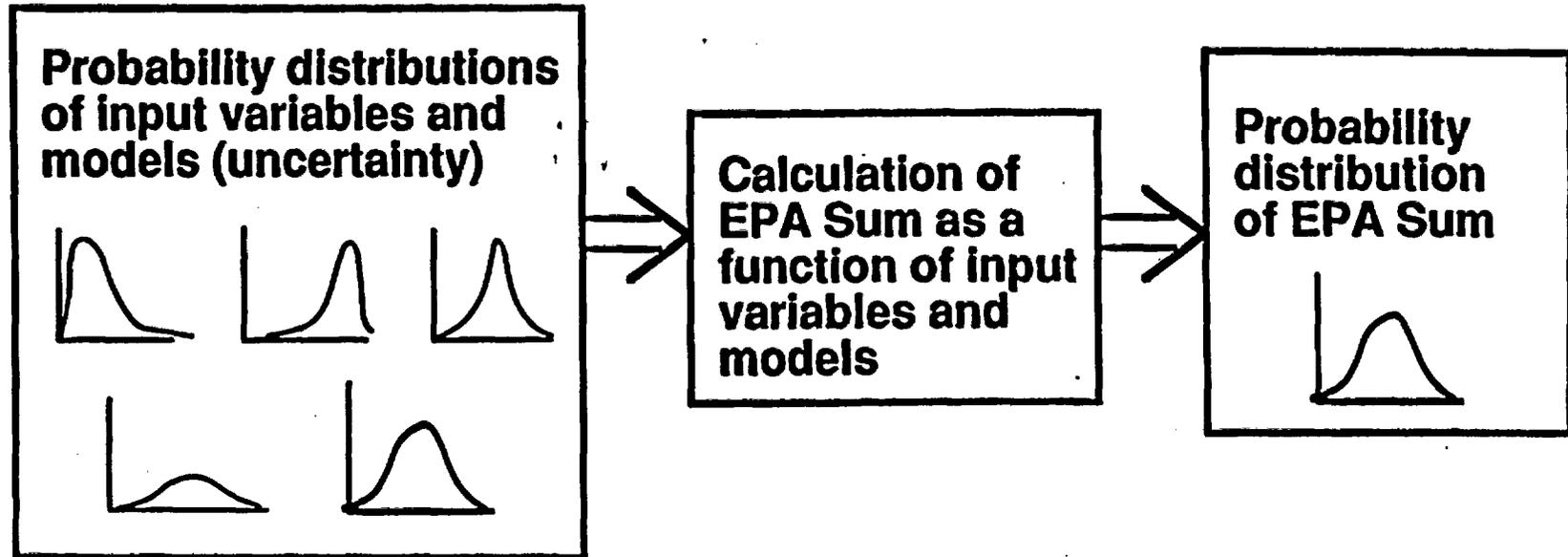
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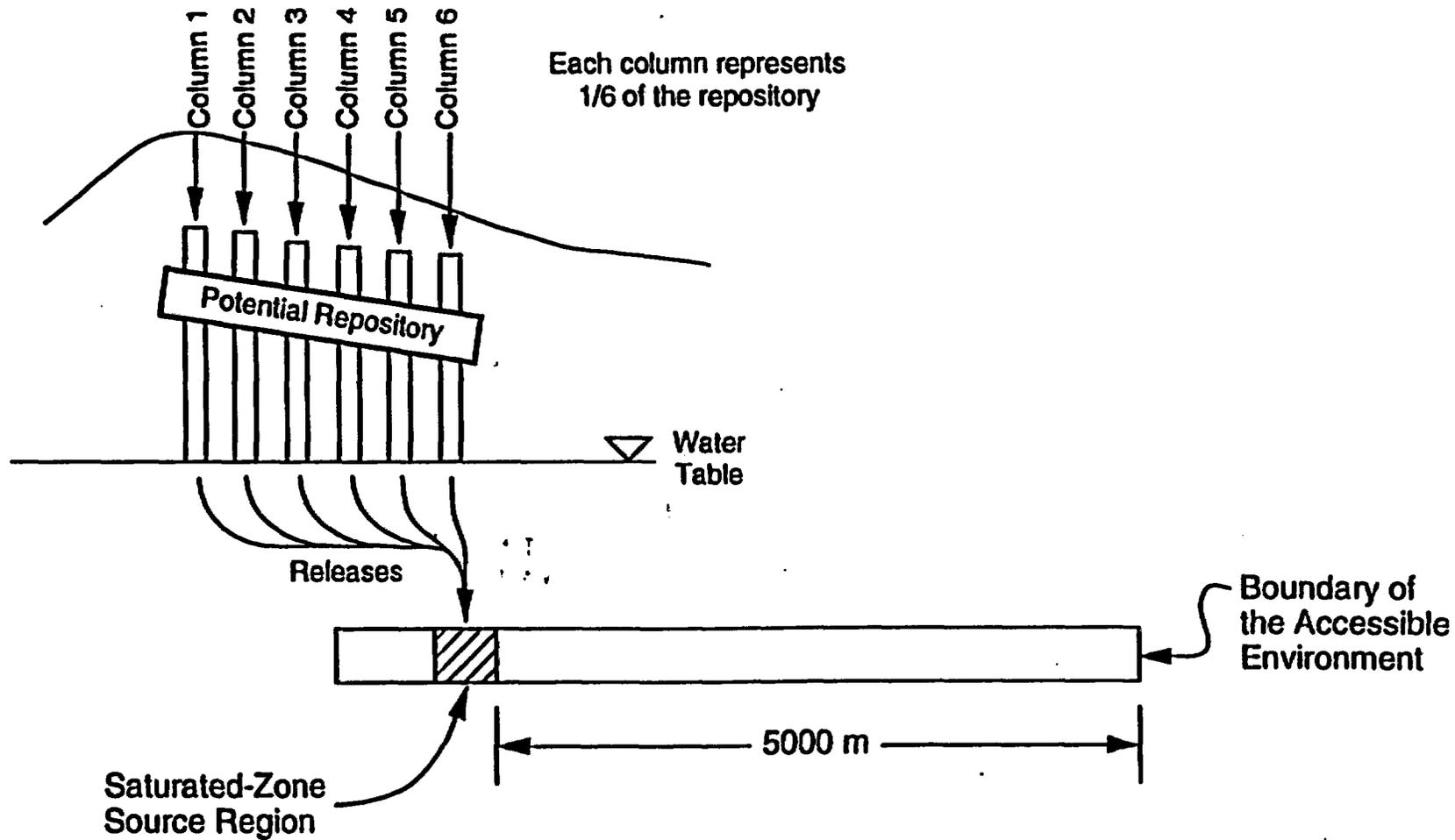
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Part One: The Setup

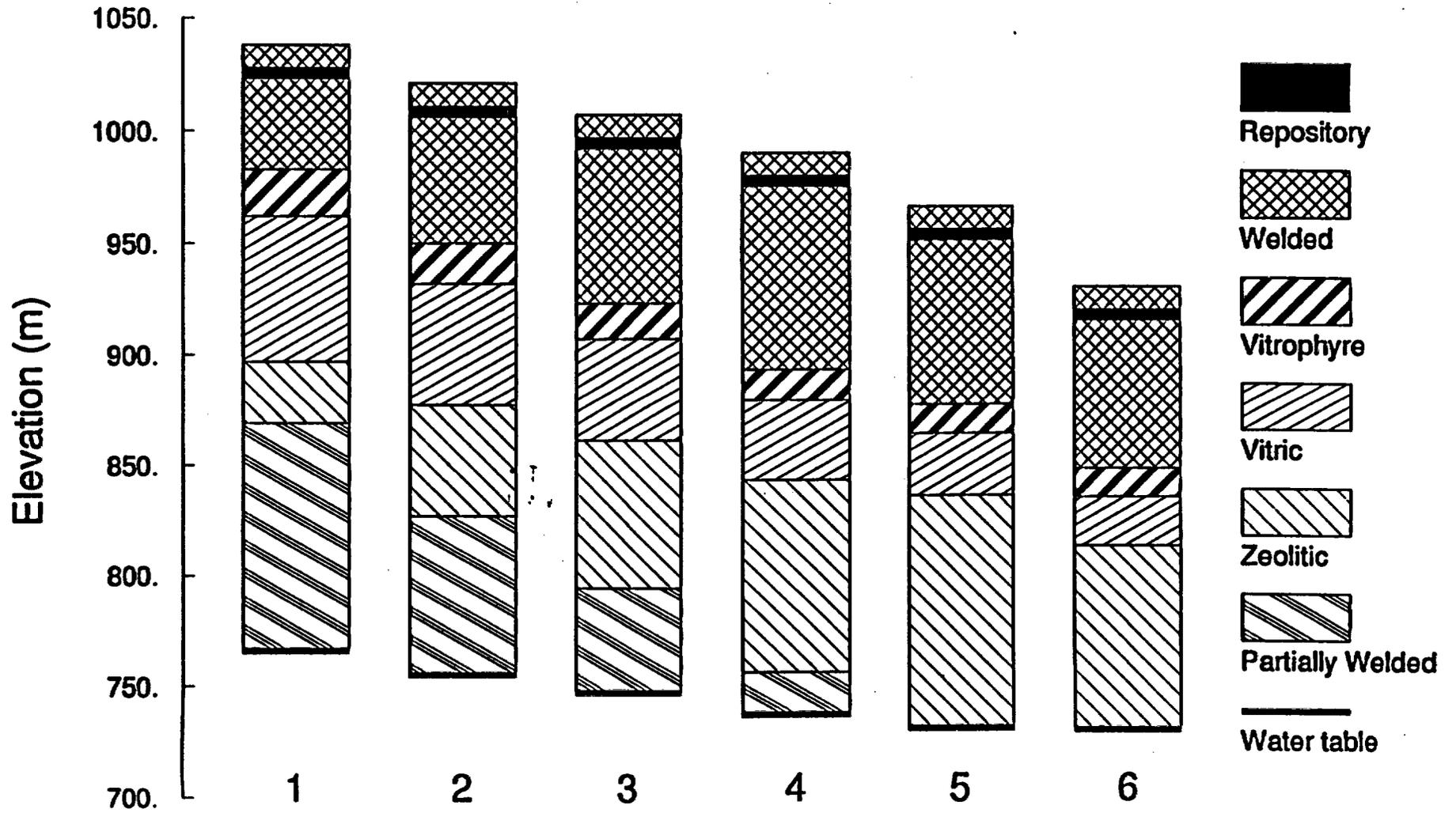
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122

The EPA regulations are *probabilistic*.
The normalized release (EPA sum) is regarded as a random variable, for which we must determine a probability distribution.





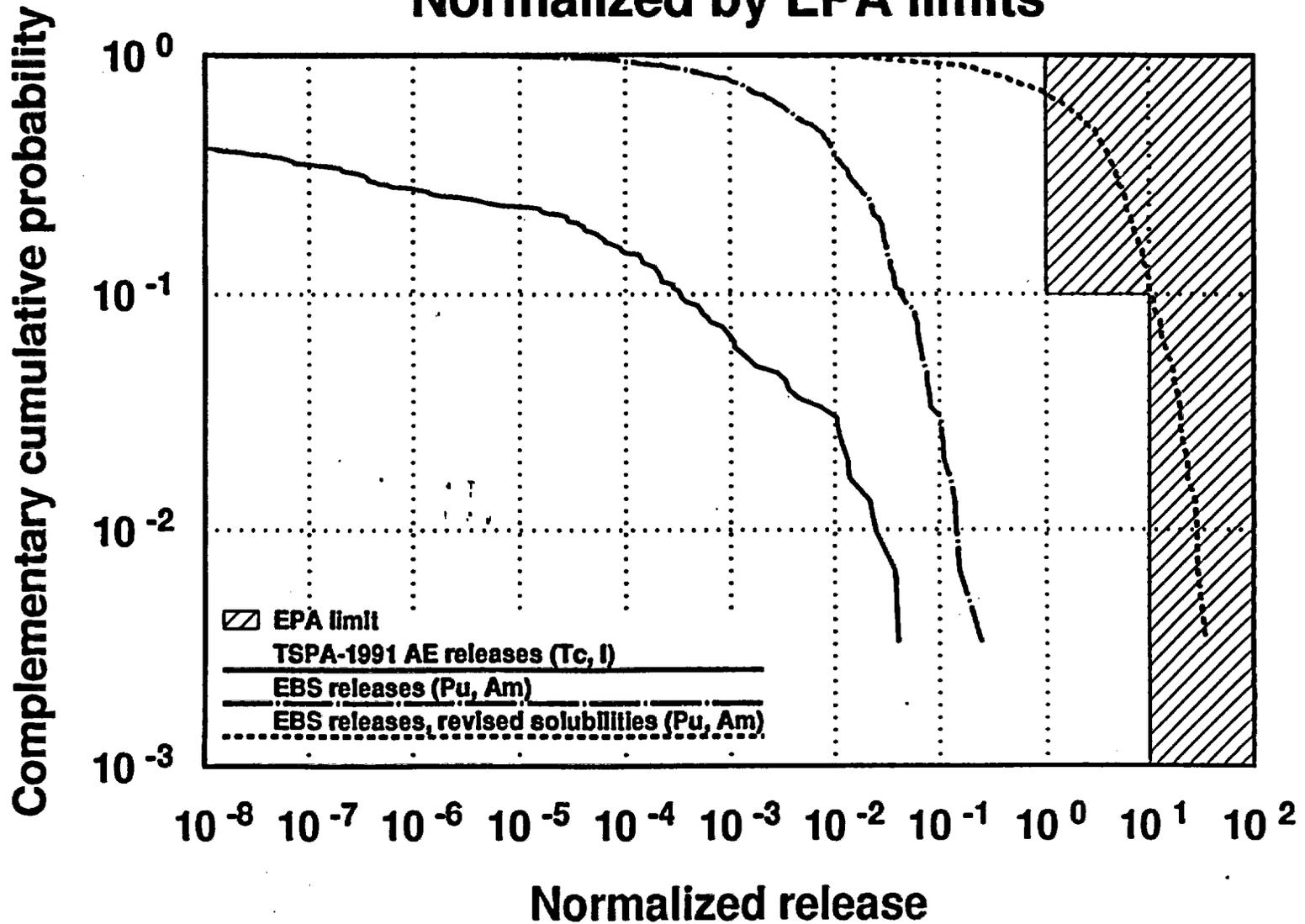
TSPA-1991 Stratigraphic Columns



Engineered Barrier System (EBS) release model for Pu & Am includes the following:

- **Thermal “dry-out” period for 300 to 1300 years**
- **Container lifetime of 500 to 10,000 years after wetted**
- **Advective and diffusive releases**
- **Solubility-limited mobilization**
- **Probability distributions for 8 important parameters**

10,000-yr Releases for TSPA Col. 6 Normalized by EPA limits

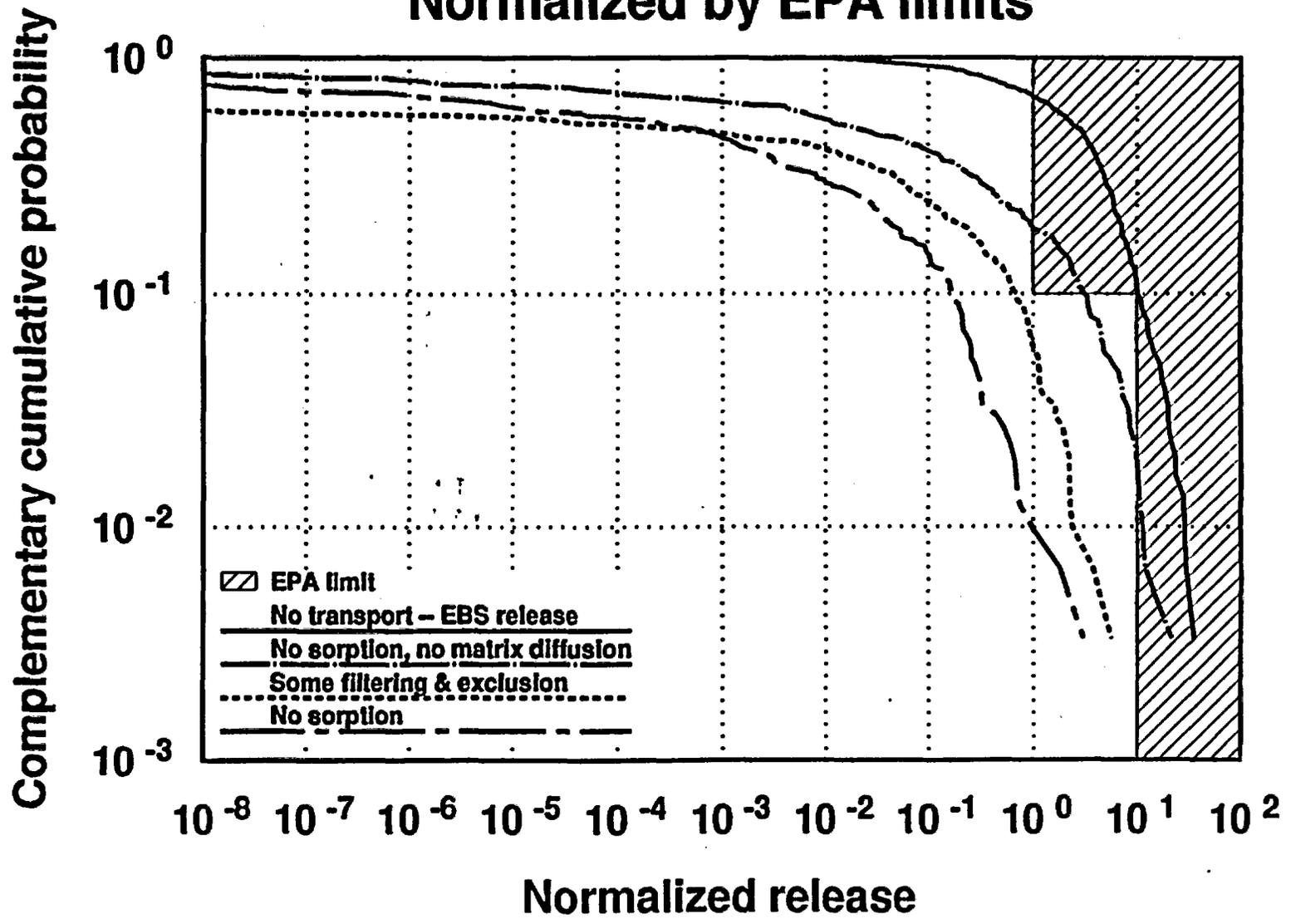


Part Two: Transport

Transport model includes the following:

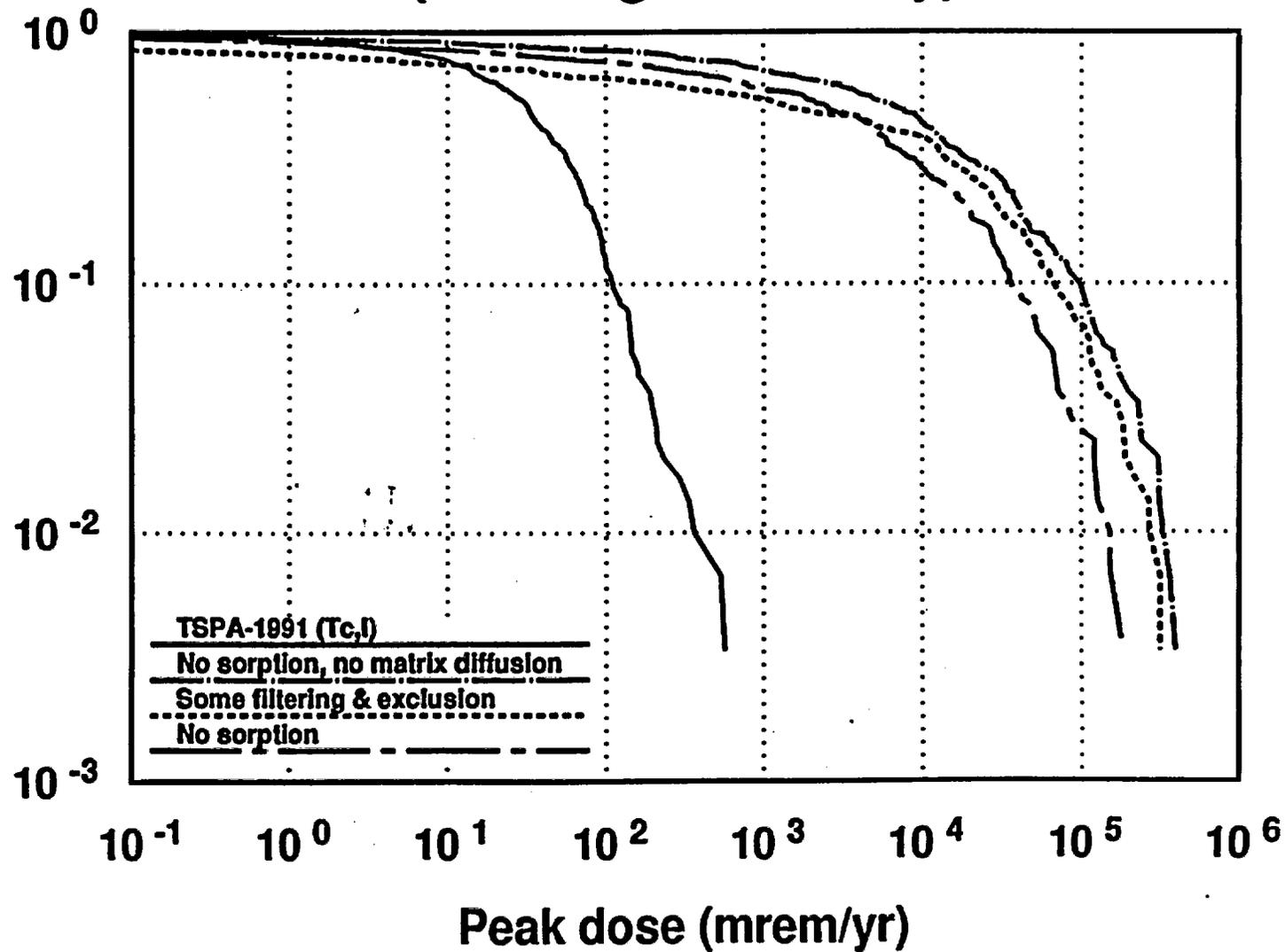
- **One spatial dimension only**
- **Steady-state water flow calculated using composite-porosity model**
- **Dual-continuum transport model
(coupled advection-dispersion equations)**
- **Advective and diffusive coupling between matrix and fracture transport**
- **Adsorption retardation modeled using K_d s**
- **Probability distributions for 45 important parameters
(plus the source-model parameters)**

Pu, Am Releases for TSPA Col. 6 Normalized by EPA limits



Pu, Am Peak Doses (Drinking water only)

Complementary cumulative probability



Part Three: Fraction Transported on Colloids

Calculation of fraction of Pu & Am sorbed to colloids (after Ogard, 1987):

- Colloid surface area estimated as

$$\frac{\chi}{\frac{4}{3}\pi r_c^3 \rho_c} \cdot 4\pi r_c^2 = \frac{3\chi}{\rho_c r_c} \quad (\chi \text{ is colloid conc. in g/l})$$

- Amount sorbed to colloids given by

$$\frac{3\chi}{\rho_c r_c} \cdot K_a \cdot C \quad (C \text{ is solute conc. in mol/l})$$

Calculation of fraction of Pu & Am sorbed to colloids (cont.):

- Fraction transported on colloids estimated as

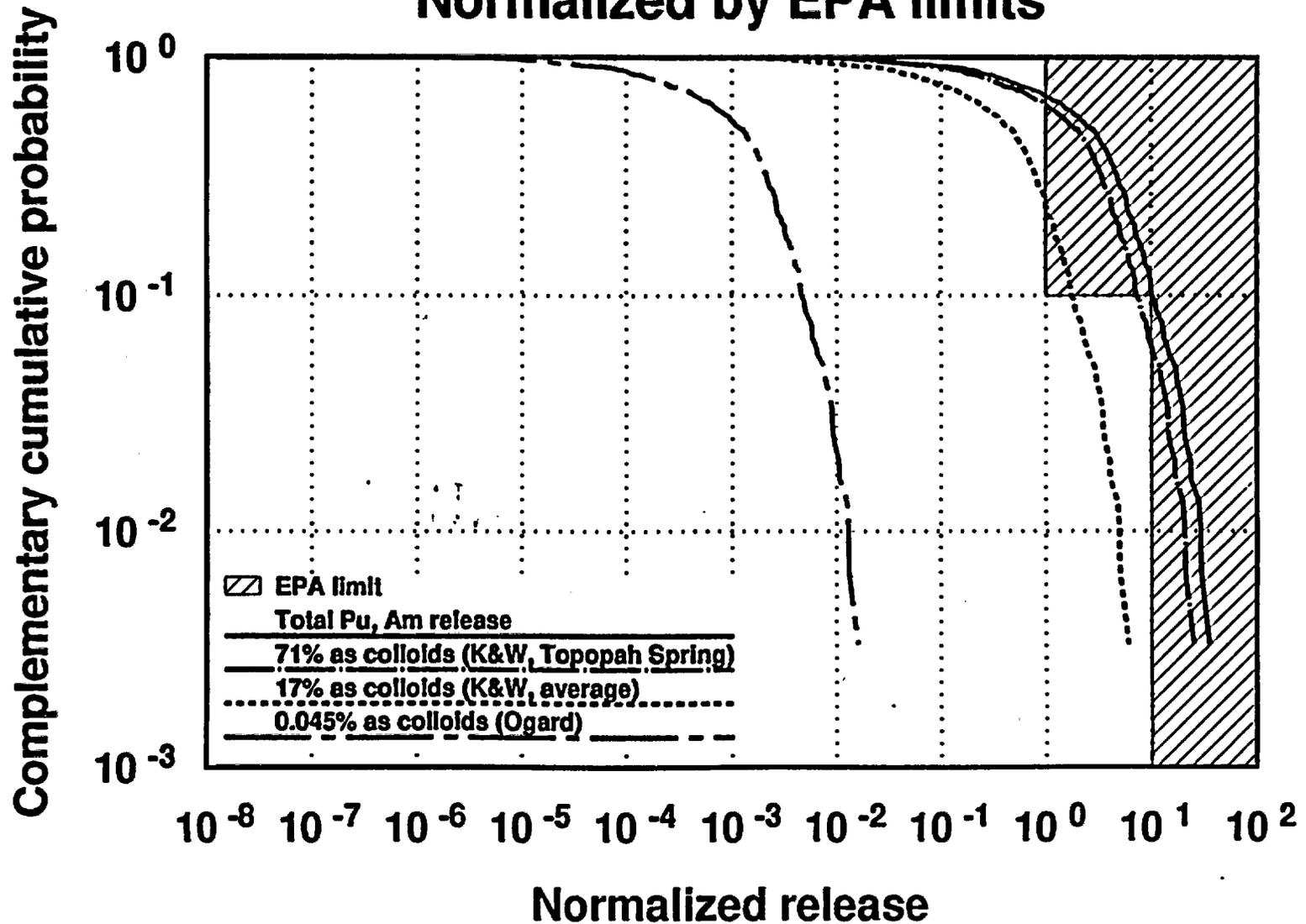
$$\frac{3\chi K_a / \rho_c r_c}{1 + 3\chi K_a / \rho_c r_c}$$

- This calculation neglects any sorption onto immobile rock.
- It also assumes irreversible sorption.

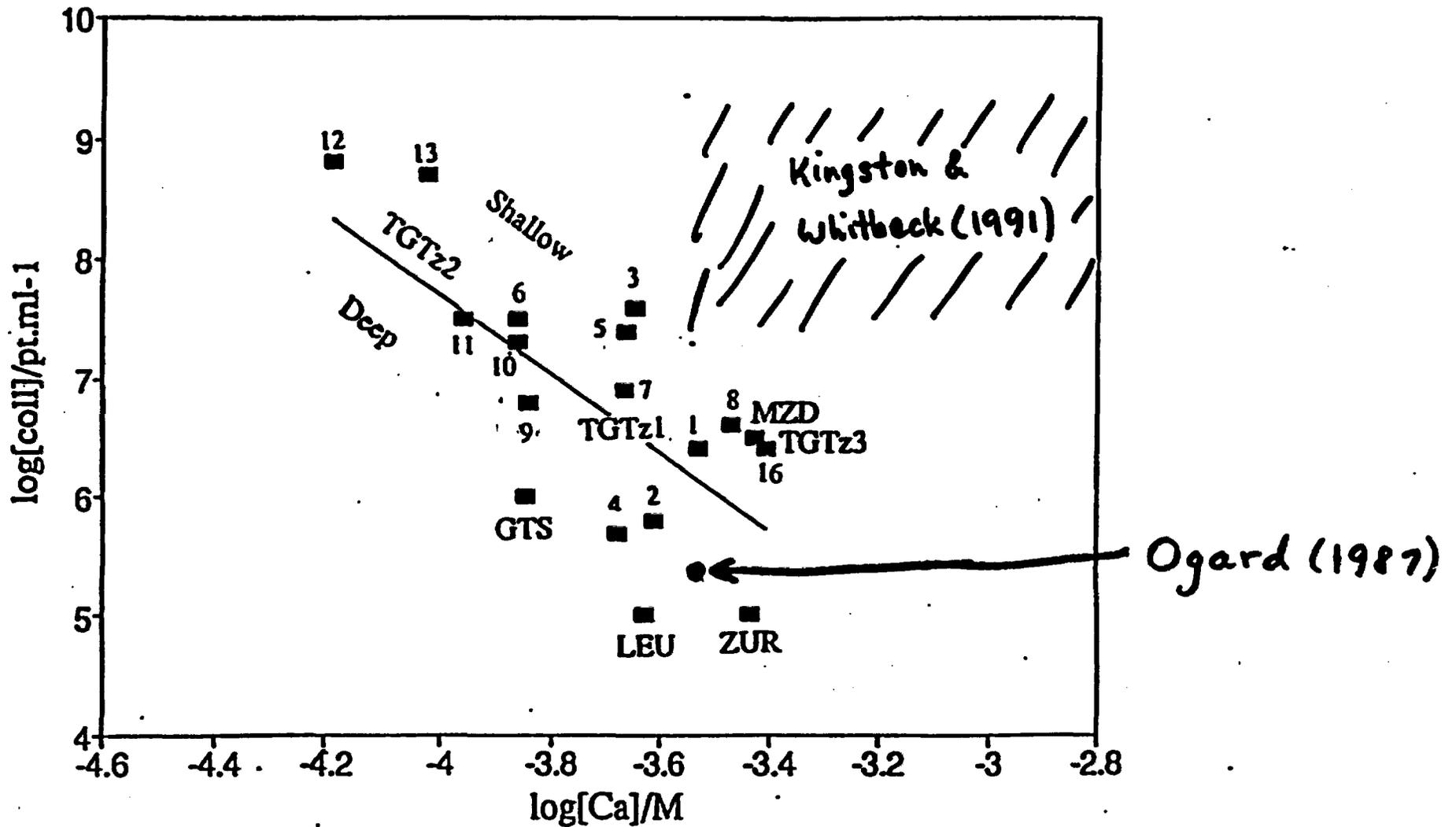
Parameters used:

- $K_a = 10^{-2} \text{ m}$ (1 mL/cm²)
(10,000 mL/g ÷ 1 m²/g)
- Colloid concentrations from
 - Ogard (1987)
 - Kingston & Whitbeck (1991)

Colloid Releases from EBS (TSPA Col. 6) Normalized by EPA limits



Plot from Degueldre (1992)



Important questions:

- **What is the colloid concentration at Yucca Mountain, and will it be increased by repository construction, EBS degradation, or future climate changes?**
- **Will the effective Pu and Am solubilities be higher because of colloid formation or other near-field conditions?**
- **Will Pu and Am sorb preferentially to colloids, or will most sorb to immobile rock?**
- **Is sorption to colloids reversible or irreversible?**

Important questions (cont.):

- **Do we need to worry about precipitation colloids (in addition to adsorption colloids)?**
- **Is matrix diffusion an effective retardation mechanism for colloids, or are they excluded from the matrix?**
- **Can colloids travel great distances at Yucca Mountain without being filtered?**

Colloid Transport Calculations with CTCN

**Yucca Mountain Site Characterization
Project Colloid Workshop**

Sante Fe, N.M., May 3-5, 1993

by

H. E. Nuttall,

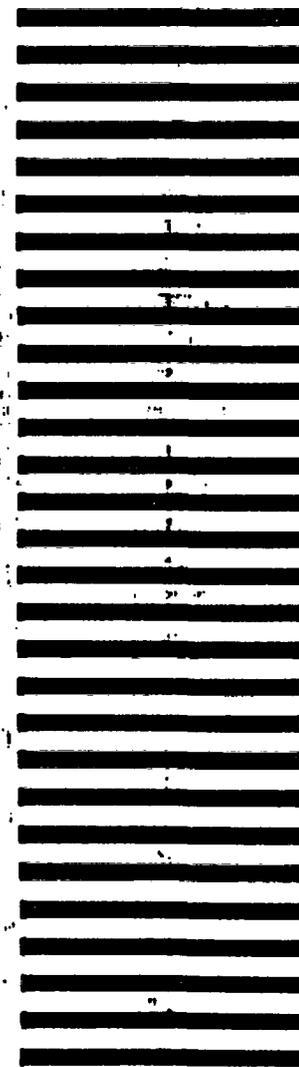
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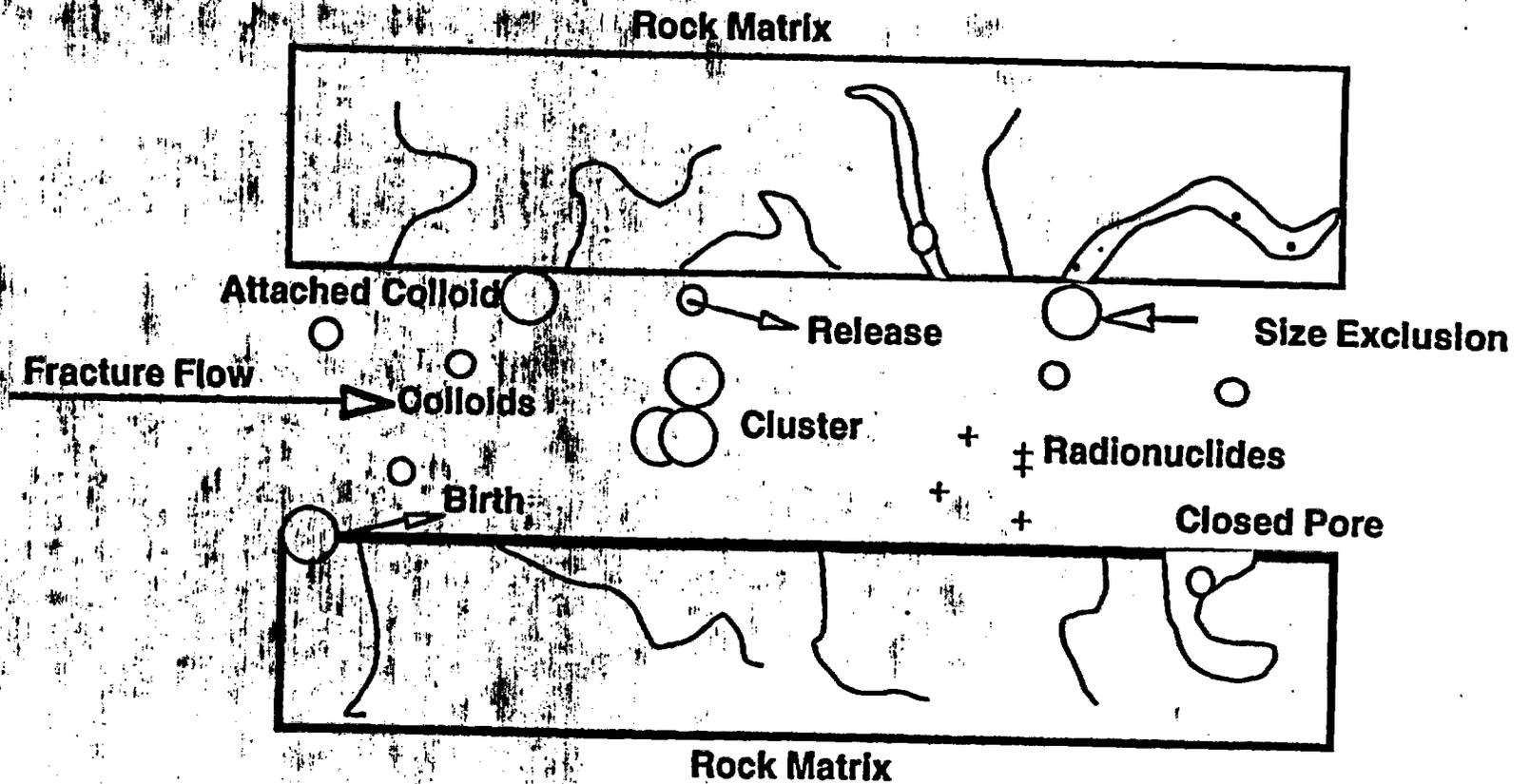
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A Model and Computer Code for Particulate Systems

• R. Jain



Colloid Transport Processes in Groundwater Flow



MODEL FORMULATION

The model requires submodels for the following phenomena:

1. Birth rate (increase from the total and subtraction)

2. Death rate

3. Growth rate

4. Migration (immigration and emigration)

5. Natural mortality (predation, disease, etc.)

6. Harvesting (commercial and recreational)

MODEL FORMULATION

It is essential to keep track of colloidal properties since they can play a crucial role in colloid transport, e.g. size, composition etc. Population Balance method treats properties as additional independent axes of the state space. These properties are assumed to be continuous.

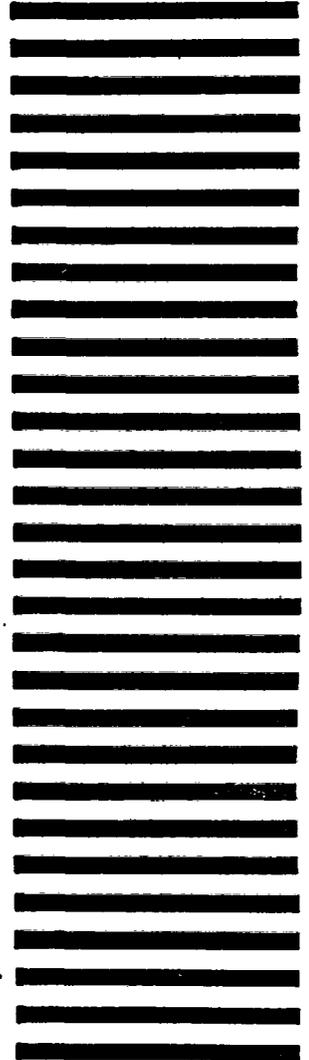
Model

- hydrology
- species balances for all distinct chemical species
- population balances for all distinct colloidal species



The Population Balance

- Hulburt and Katz (1964) and Randolph (1964)
- mass balance equation conserving number of particles (colloids)
- additional property axes
- dependent variable = number density
- + species mass transport + energy and momentum balance



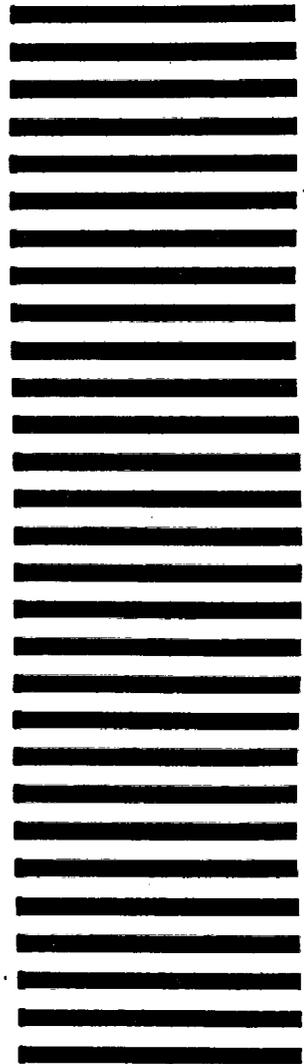
Particle-Number Continuity Equation

- Accumulation = Input - Output + Generation
- Population balance for each colloidal species 'i'

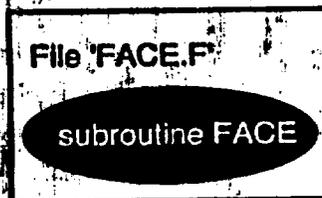
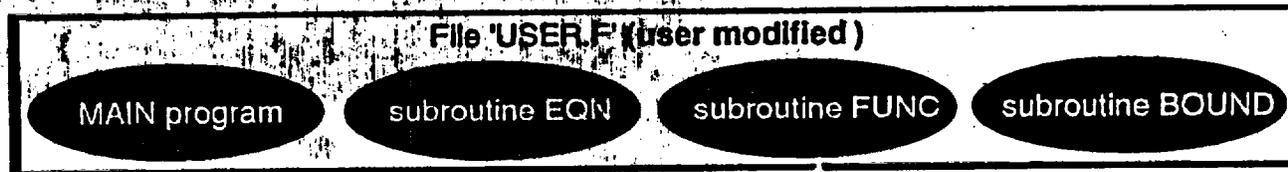
$$\frac{\partial \psi_i}{\partial t} + \nabla \cdot (\vec{v} \psi_i) - D \nabla^2 \psi_i + \sum_{j=1}^m \frac{\partial (\alpha_{ji} \psi_j)}{\partial \xi_j} + D_i - B_i = 0$$

Computer Code

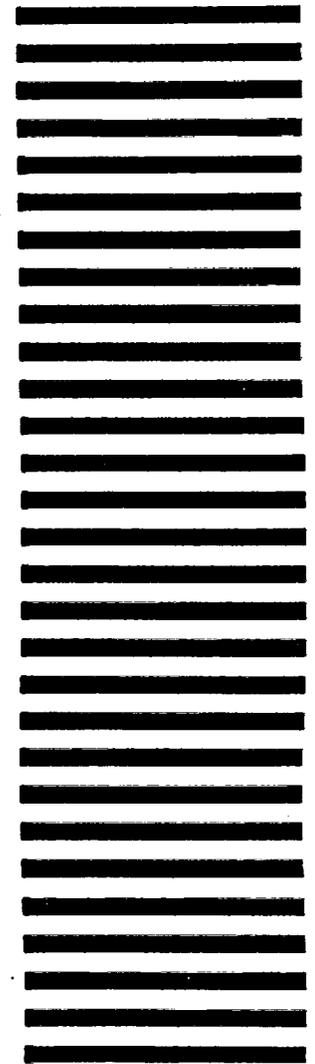
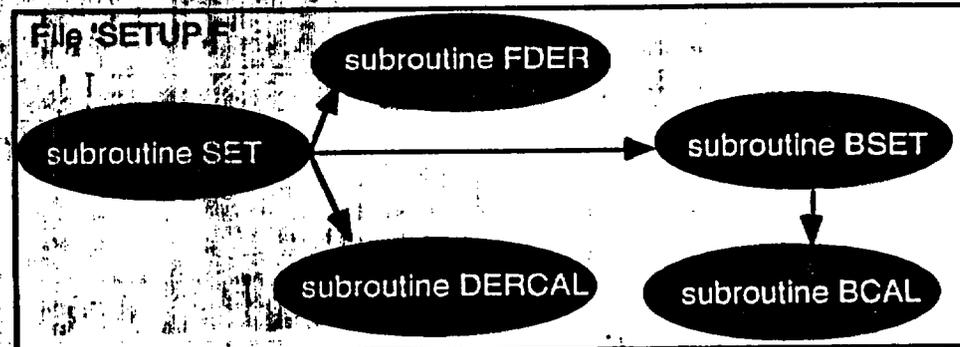
- solve PBE with mass, energy, momenta equations
 - solves any 2nd order differential system
- up to four independent axes
- wide range of boundary conditions and submodels
- choice of finite-difference discretizations



Structural Overview



ODE solver
LSODES / LSODPK



ELLIPTIC EQUATION

The problem is an elliptic PDE that represents a parallel plate capacitor by a unit by obtaining object. The PDE is

$$\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} - 6xy e^x e^y (xy + x + y - 3) \quad 0 \leq x \leq 1, 0 \leq y \leq 1$$

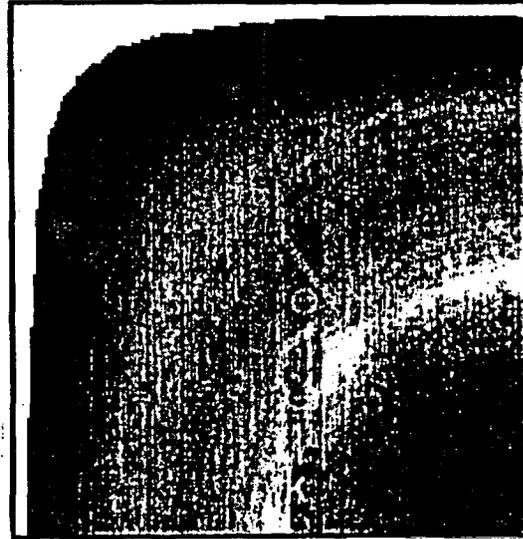
Boundary and Initial Conditions

- 1. $u(0, y) = 0$
- 2. $u(1, y) = 0$
- 3. $u(x, 0) = 0$
- 4. $u(x, 1) = 0$
- 5. $u(x, y) = 0$

ELLIPTICAL EQUATION



analytical solution



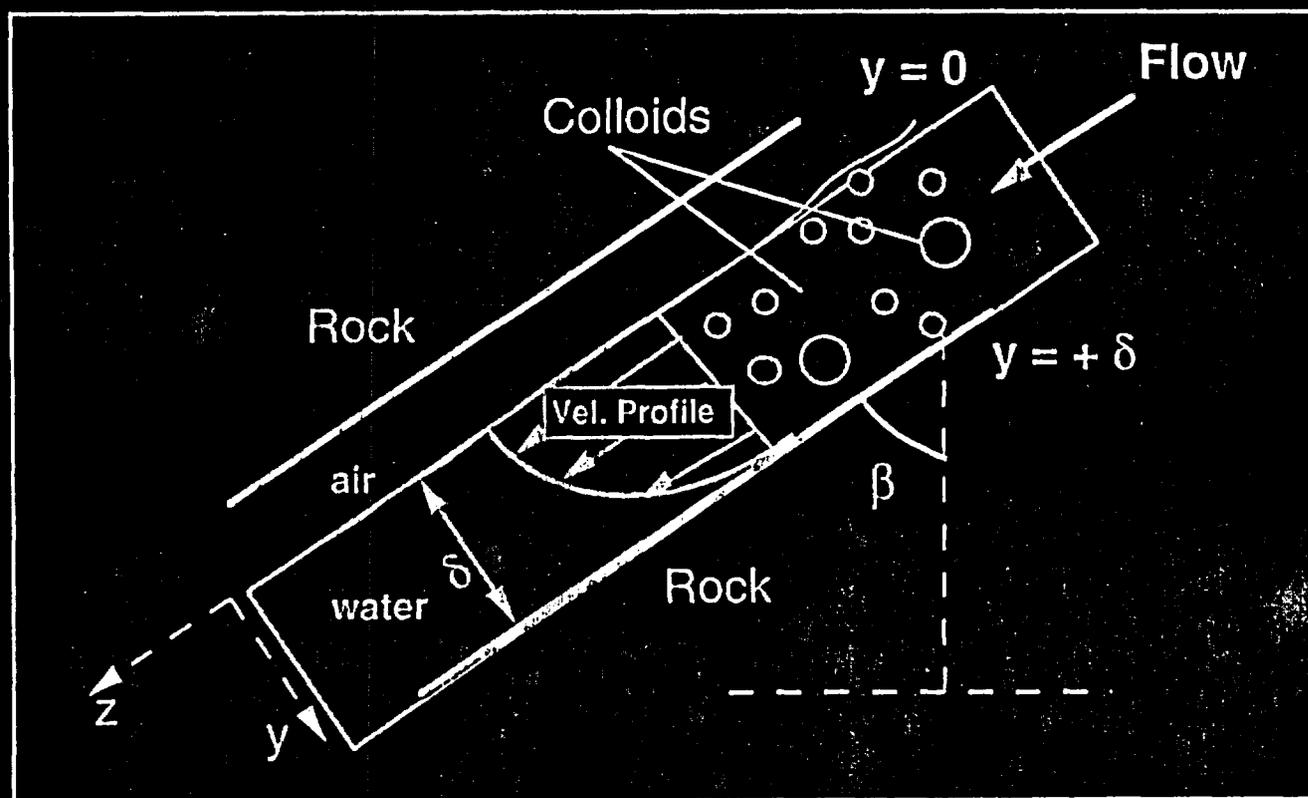
numerical solution

$u = 0$

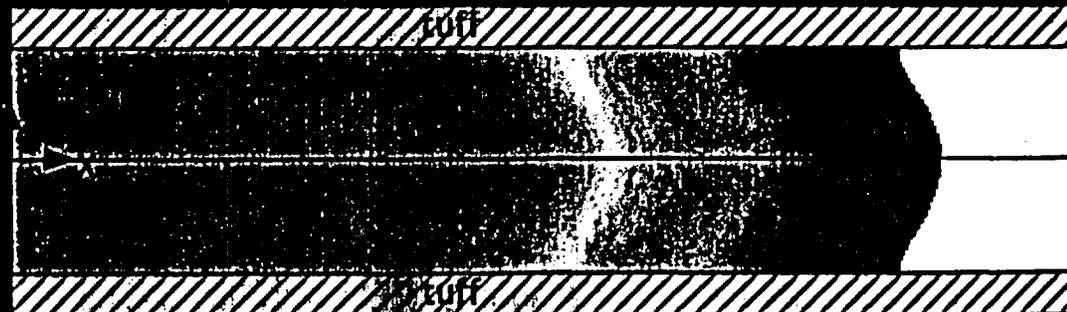
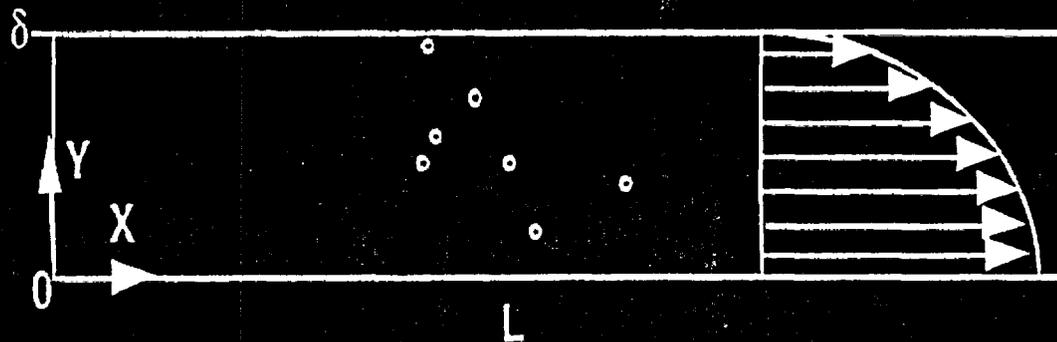
SCALE

$u = 1$

COLLOID TRANSPORT IN AN UNSATURATED FRACTURE

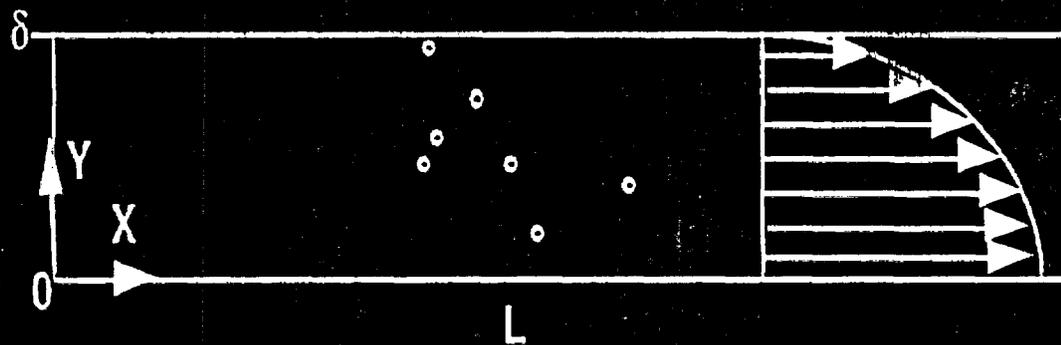


Prüfung in Dämmtechnik

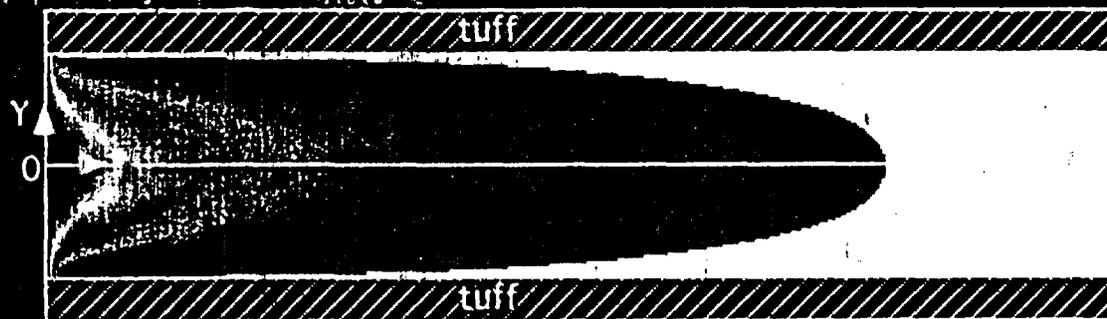


1 | **ISCALE** |

Prandtl's Problem

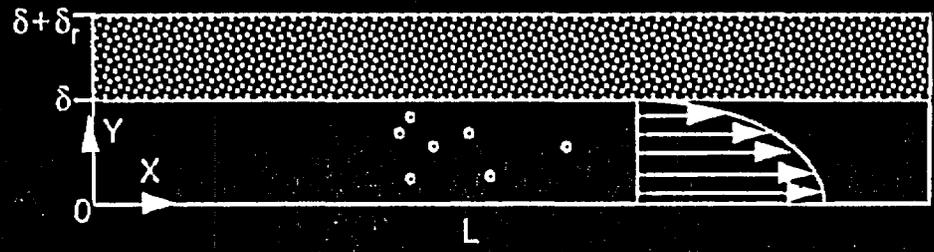


Prandtl's Problem

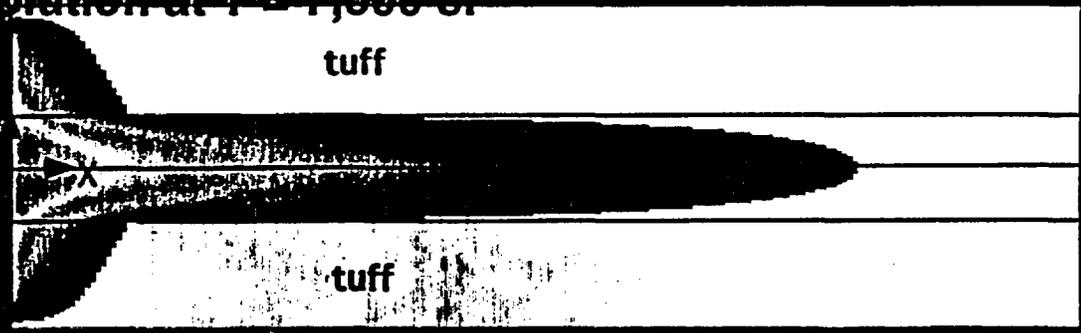


$u = 0$ SCALE $u = 1$

Figure 10: Diagram

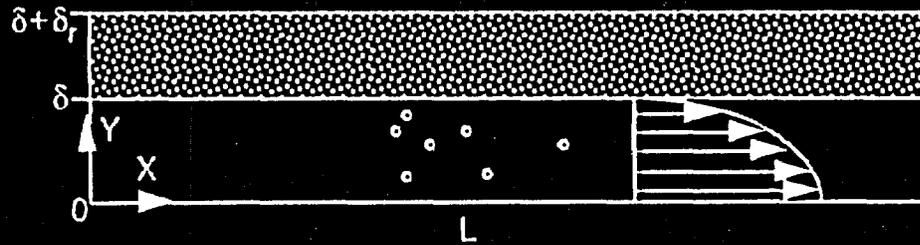


Separation at $\bar{T} = 7,800$ K.

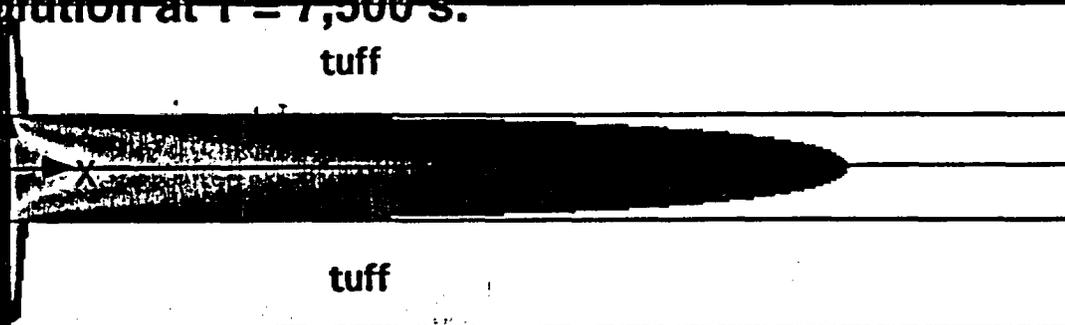


SCALE 1:1

Problem Domain

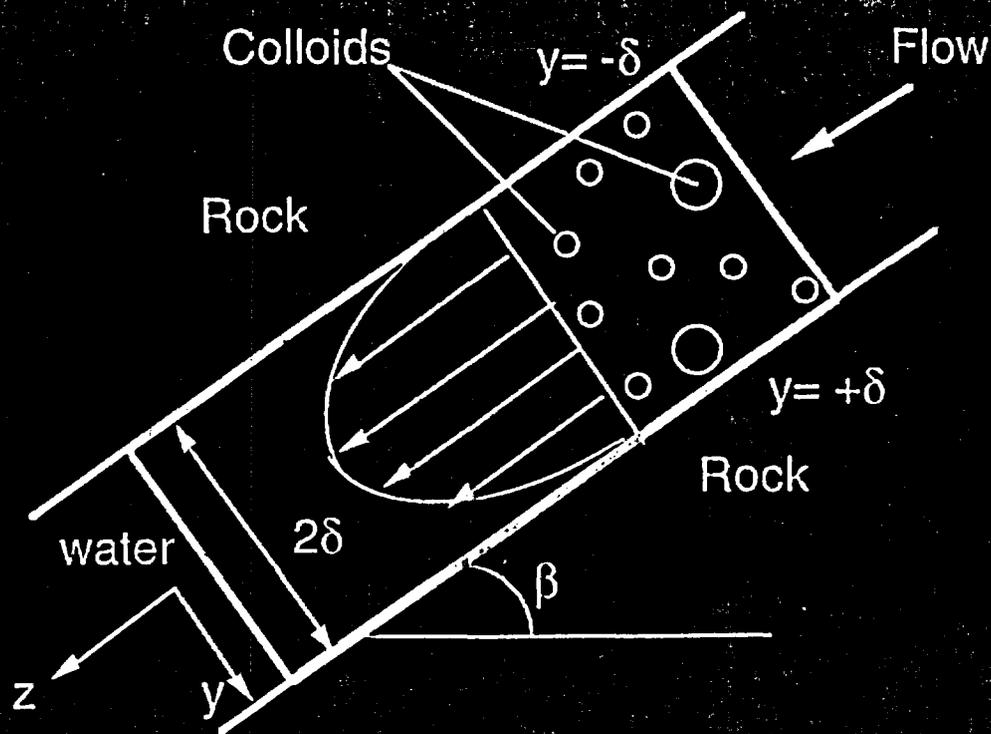


Simulation at $t = 7,500$ s.



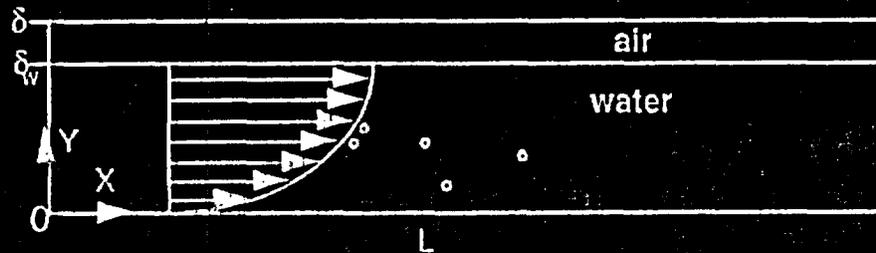
1 | SCALING

COLLOID TRANSPORT IN A SATURATED FRACTURE



UNSATURATED FLOW

The first two cases are analogous to that for saturated flow except that the problem domain is as shown below

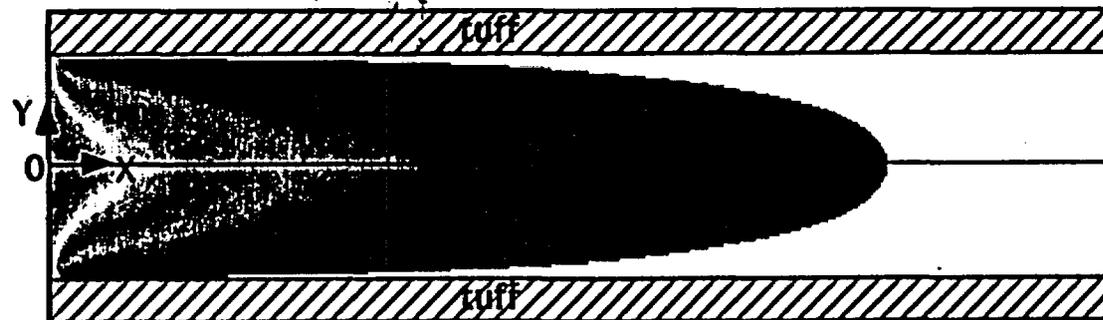
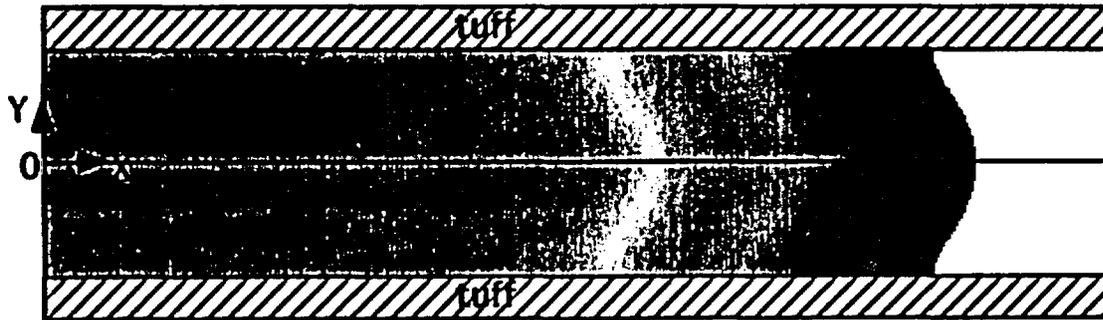


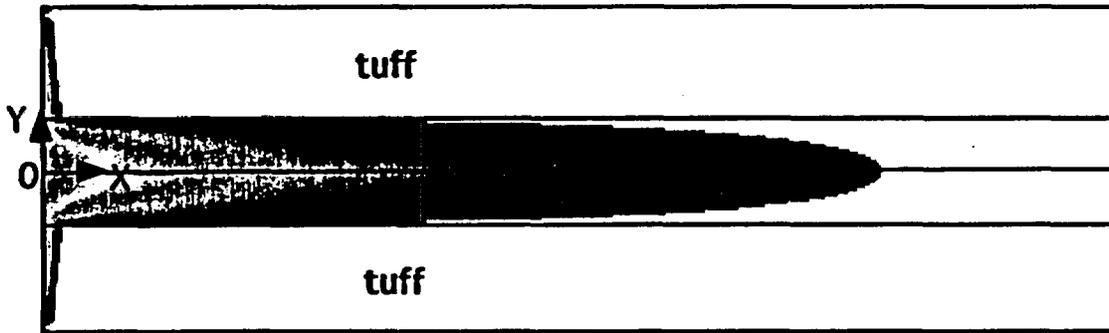
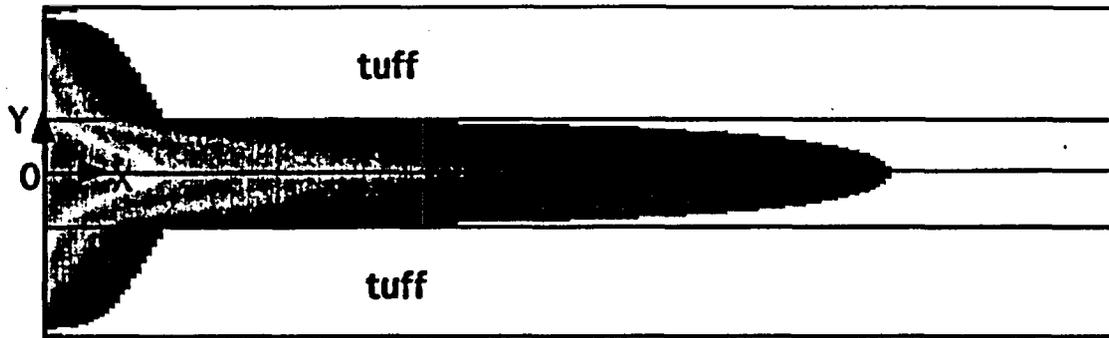
computational 1-2-300's



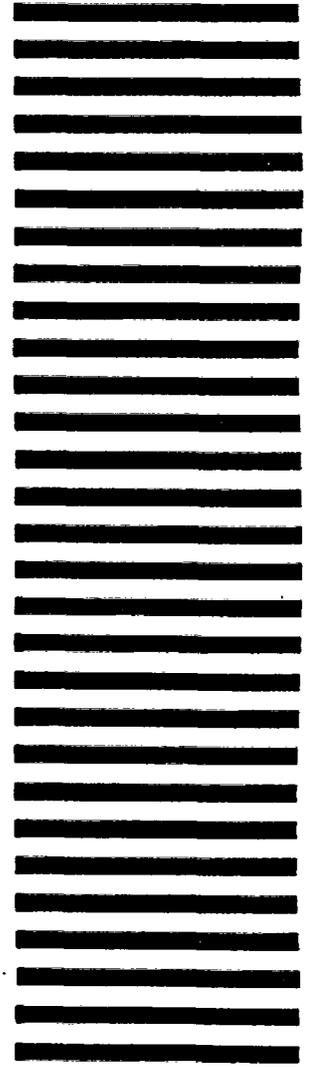
SCALE

Applications

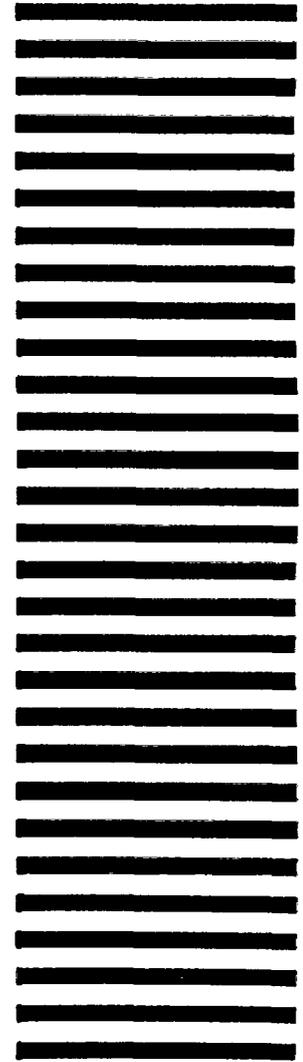
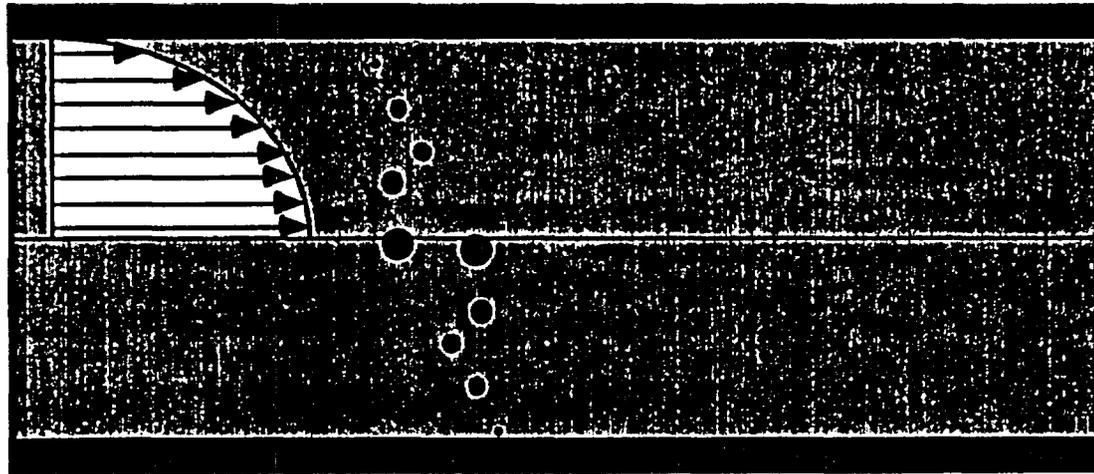




u = 0 [**SCALE**] u = 1



Example 2 : Fracture Problem



Fracture Simulation - 2D and Particle Size

Equation:

$$\frac{\partial u}{\partial t} = - (v_z)_{\max} \left(1 - \left(\frac{y}{\delta} \right)^2 \right) \frac{\partial u}{\partial z} + D_z \frac{\partial^2 u}{\partial z^2} + D_y \frac{\partial^2 u}{\partial y^2}$$

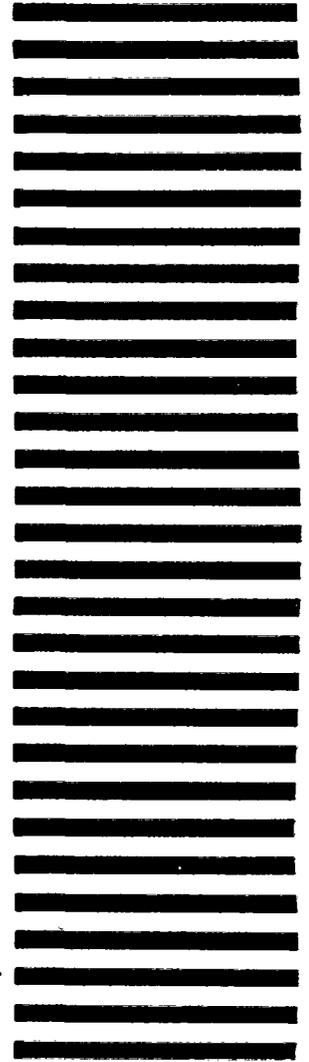
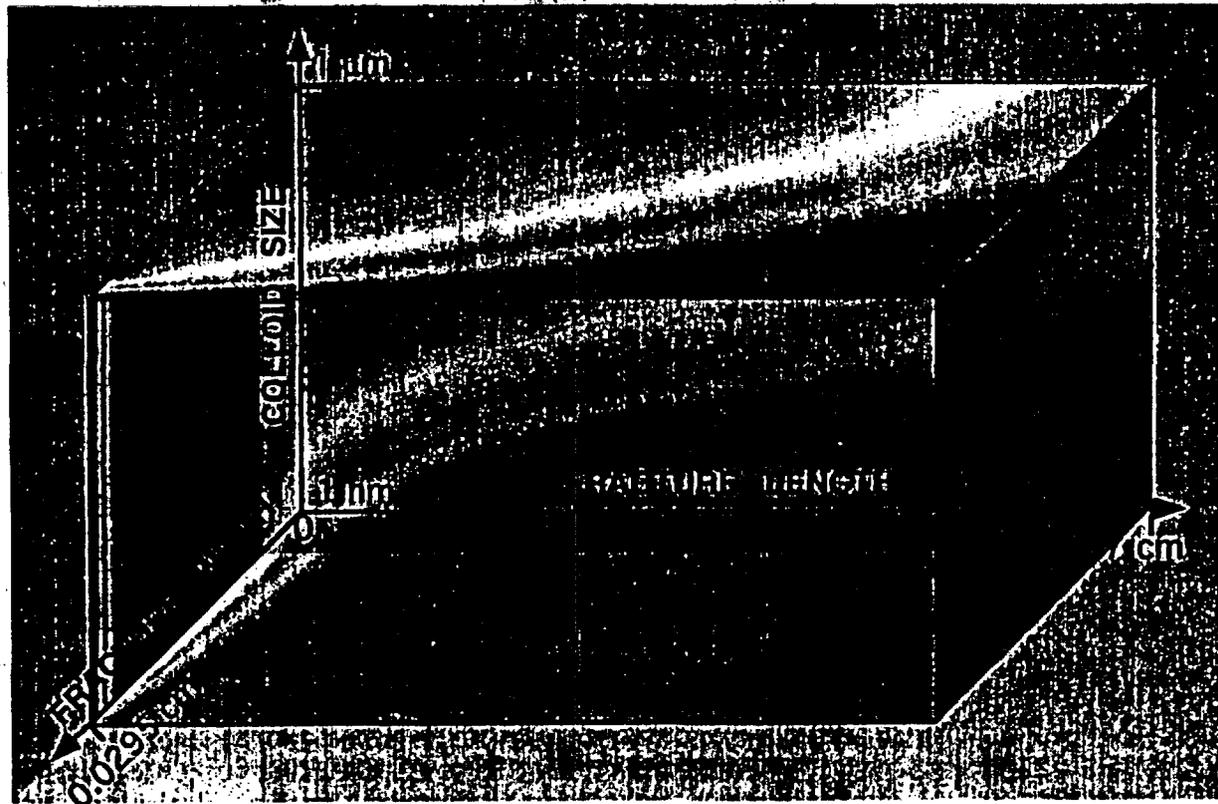
- Initial Conditions :

$$u(x, y, z) = 0$$

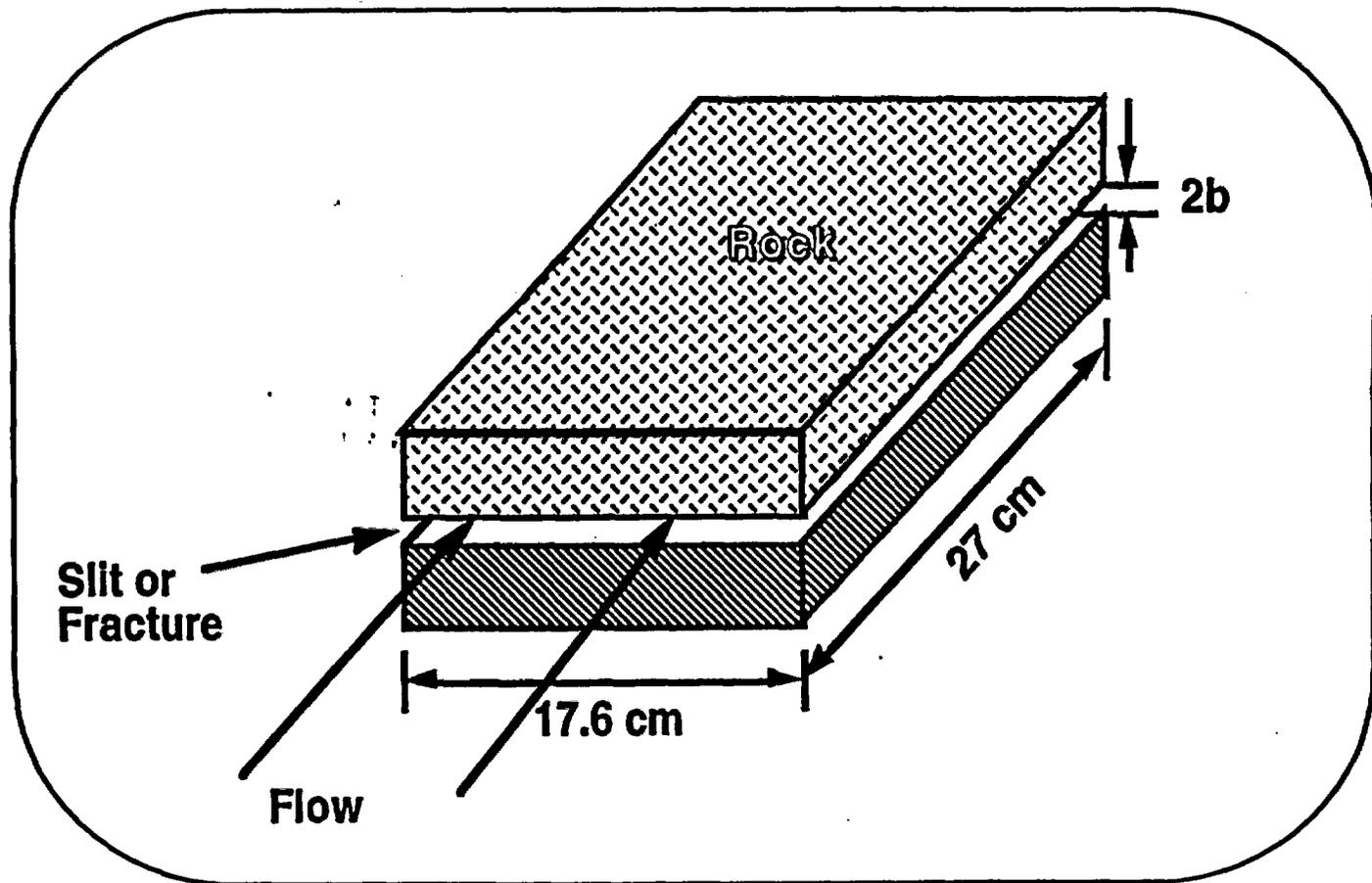
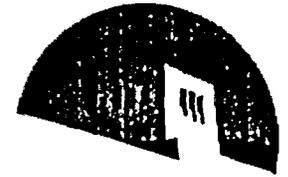
- Boundary Conditions :

$x = 0$	no boundary Condition	(size axis)
$x = 1$	no boundary Condition	(size axis)
$y = 0$	$\partial u / \partial y = 0$;	$y = \delta, u = 0$ (width axis)
$z = 0$	$u = 1.0$;	$z = 12, u = 0$ (length axis)

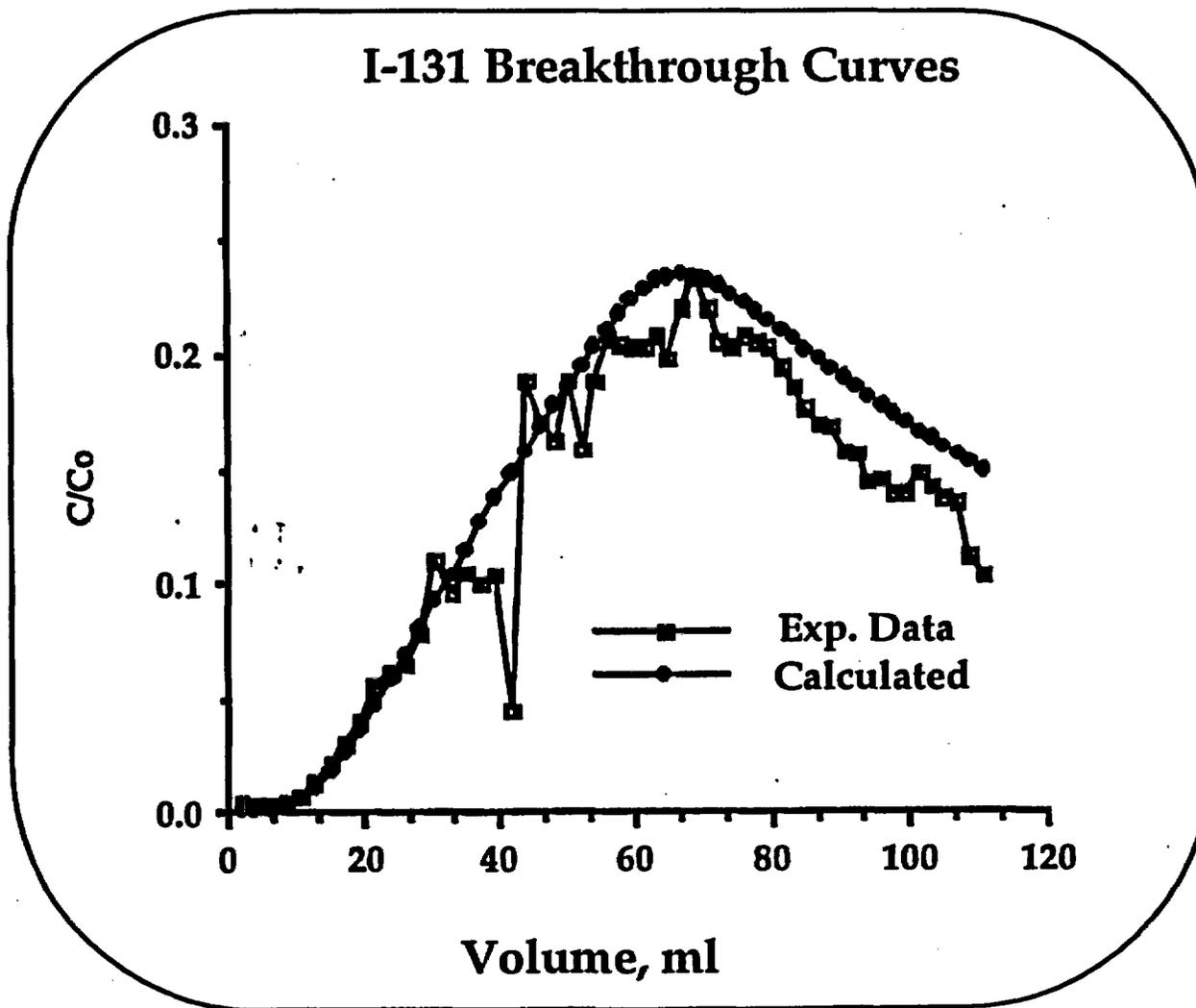
Colloidal Flow in Rectangular Fractures



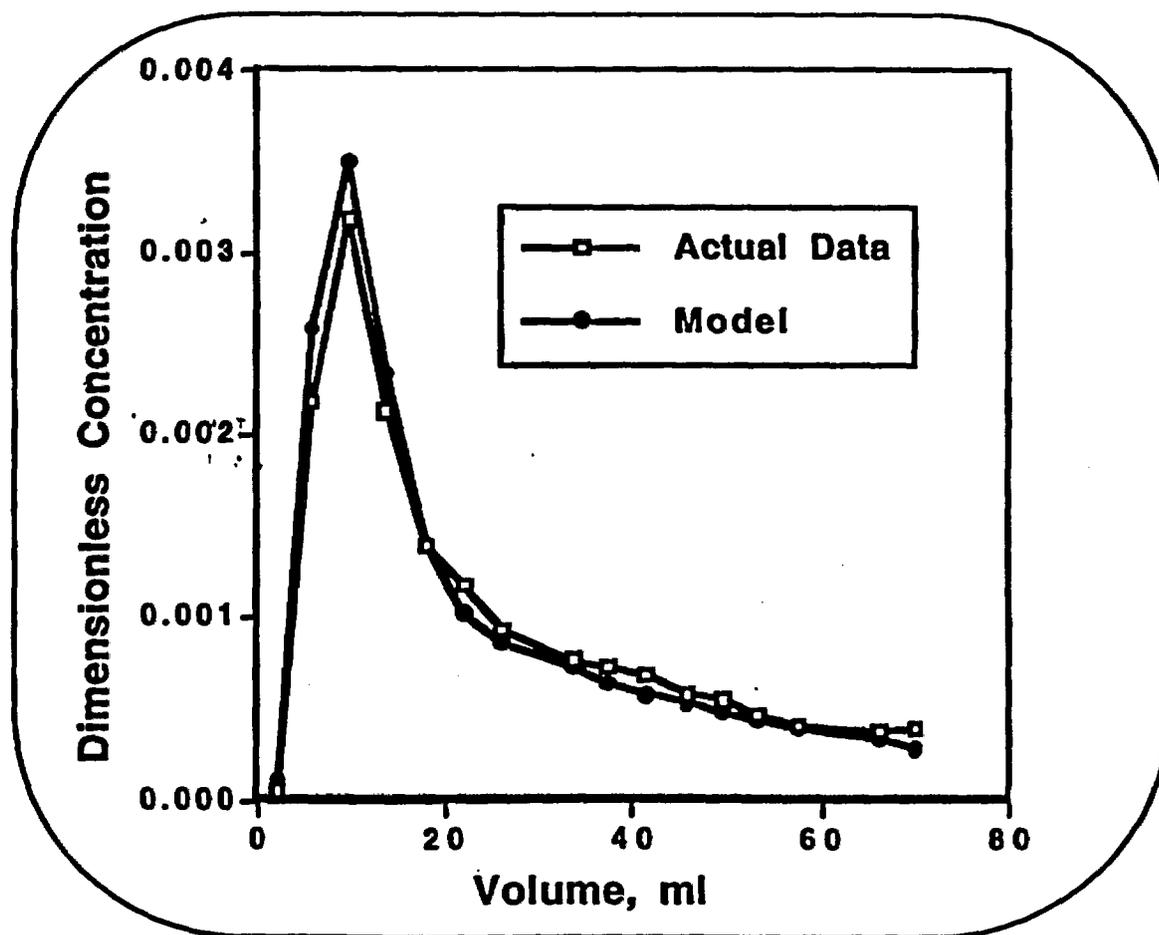
Fracture Schematic Diagram



I-131 Breakthrough Curve



Comparison of Model to Data for (3) Reversible Reactions



Single Fracture Colloid Model for Rundberg Experiments

Fluid Phase

$$\frac{\partial c}{\partial t} = -v \frac{\partial c}{\partial x} + D \frac{\partial^2 c}{\partial x^2} - \{ \text{three path reaction} \}$$

$$\text{Reaction rate} = [(k_i)(f_i)c - (k'_i)c'_i]$$

Solid Phase Interface

$$\frac{dc'_i}{dt} = (d/2)[(k_i)(f_i)c - (k'_i)c'_i]$$

Schematic diagram of apparatus

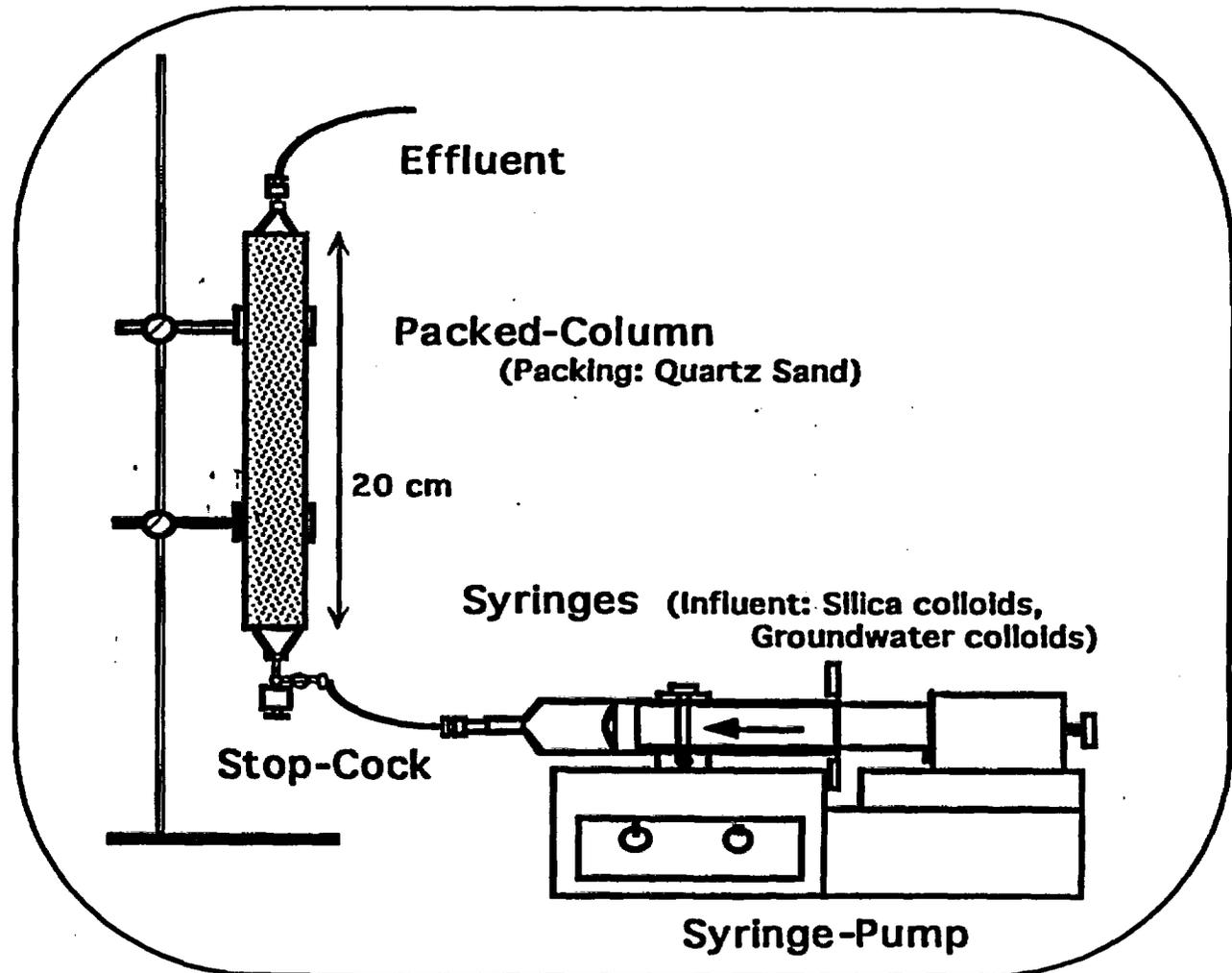
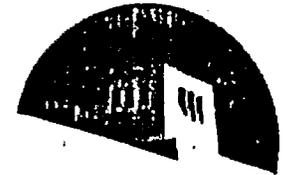
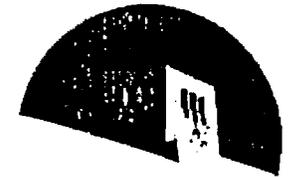


Table of Column Experiments



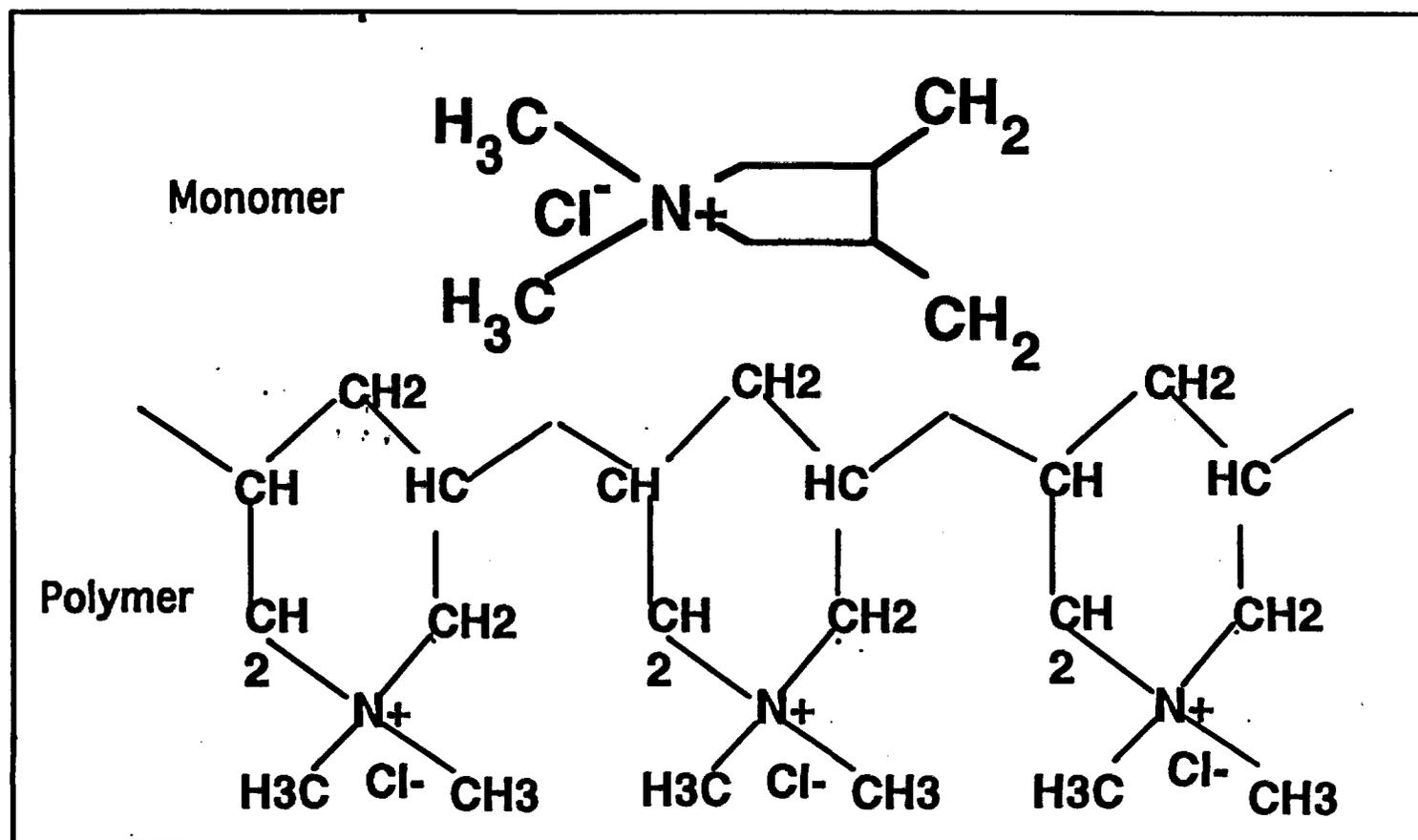
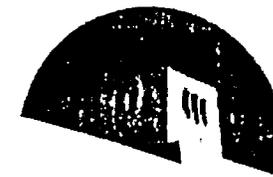
Packing	Pretreatment	Suspension
<i>Quartz</i>	Without CATFLOC	Silica Colloids in DI water
<i>Quartz</i>	With CATFLOC	Silica Colloids in DI water
<i>Quartz</i>	Without CATFLOC	Mortand Canyon colloids
<i>Quartz</i>	With CATFLOC	Mortand Canyon colloids
<i>Core from site</i>	Without CATFLOC	DI water

Characterization of Materials

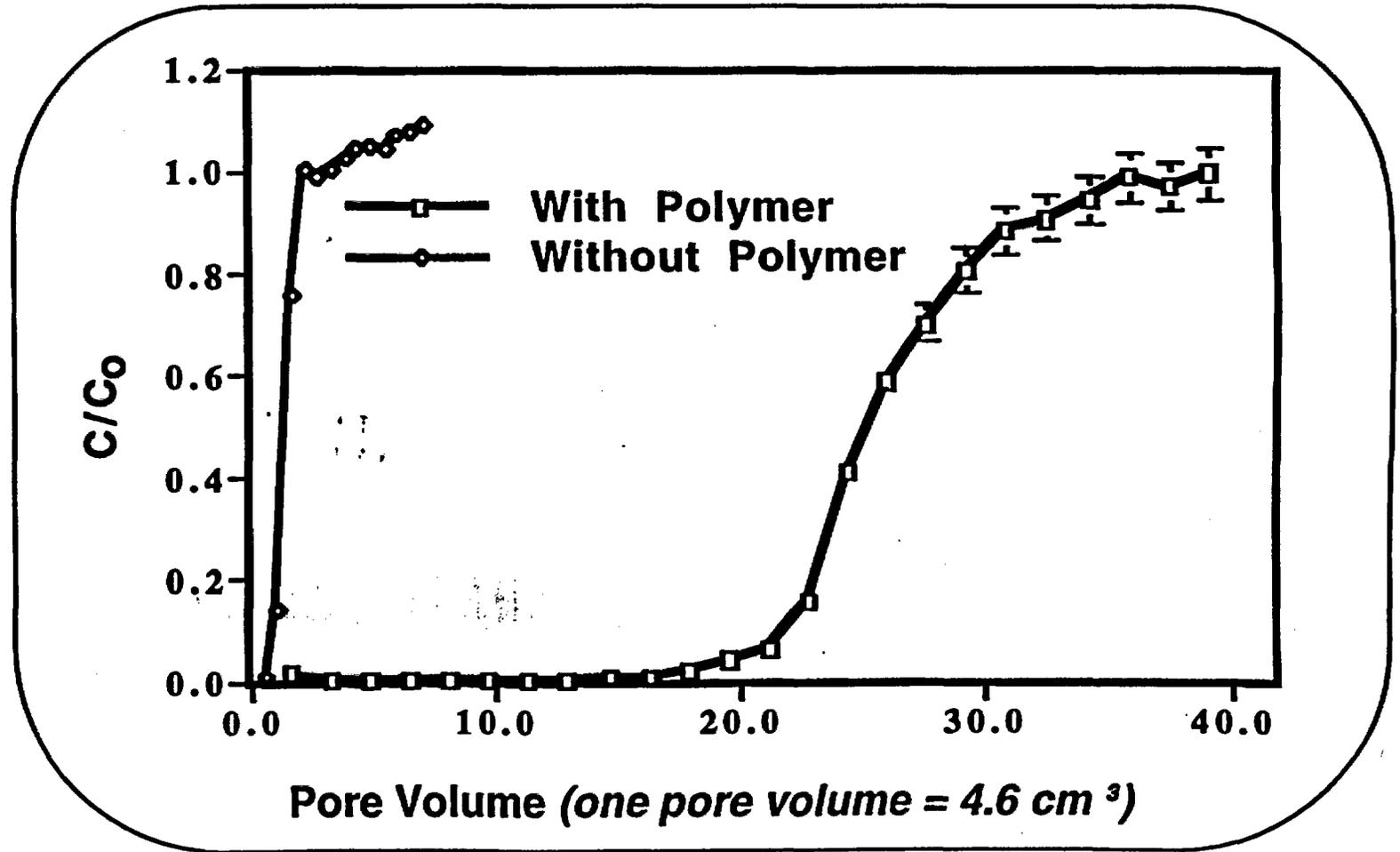
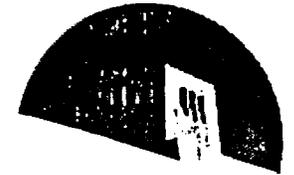


	Size (Microns)	Zeta Potential (mV) (In ground water, Well MCO-6B)	Zeta Potential (mV) (In DI water)
Colloidal Silica	0.300	- 42.25	- 66.18
Quartz sand	200 - 450	- 25.89	- 33.97
Ground Water (well MCO-6B)	1.778	- 18.56	—
Polystyrene Latex	0.746	- 34.72	- 41.83
Core Sample	0.1 - 50	- 14.53	- 30.19

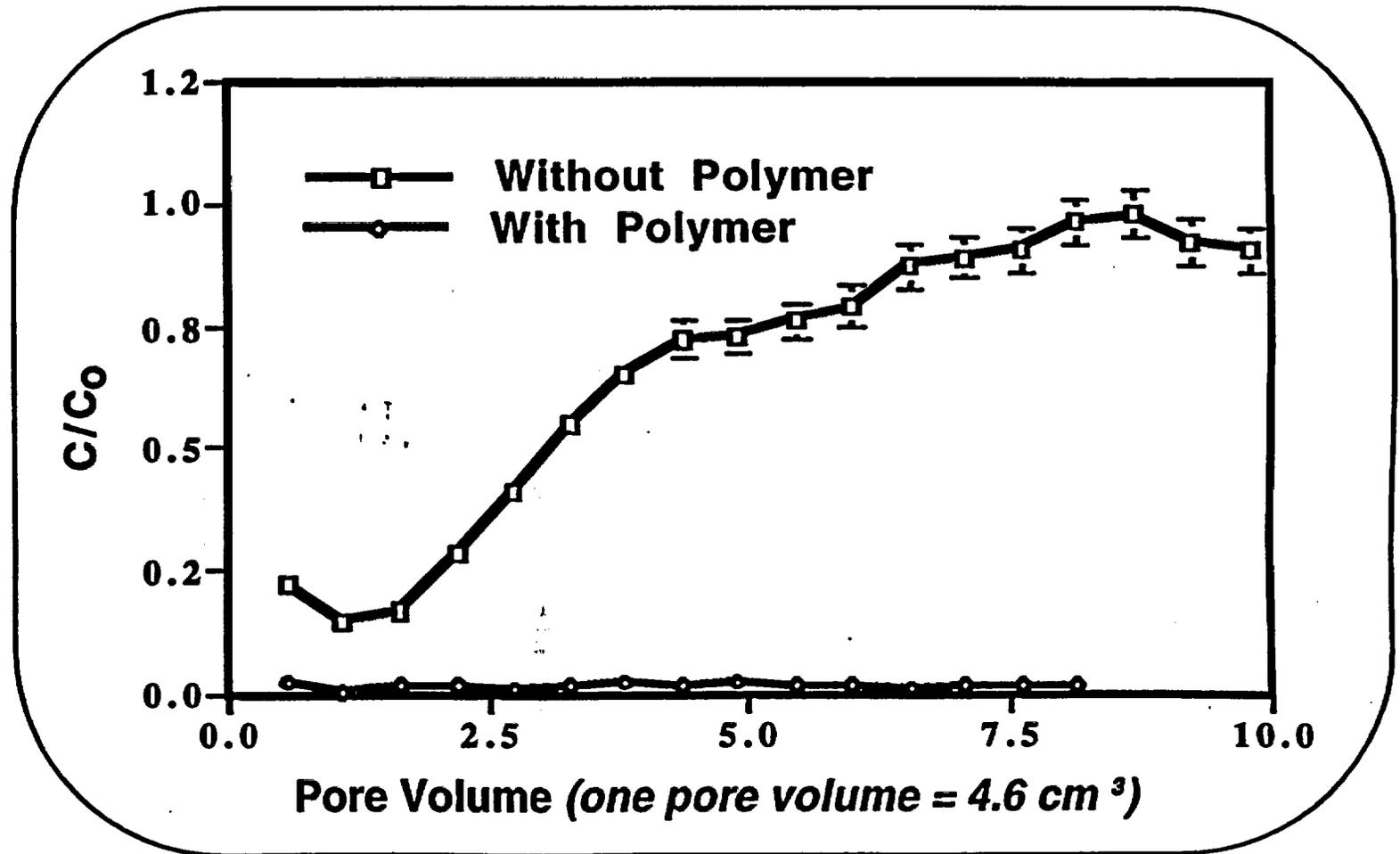
Polyelectrolyte (CATFLOC) Chemical Structure



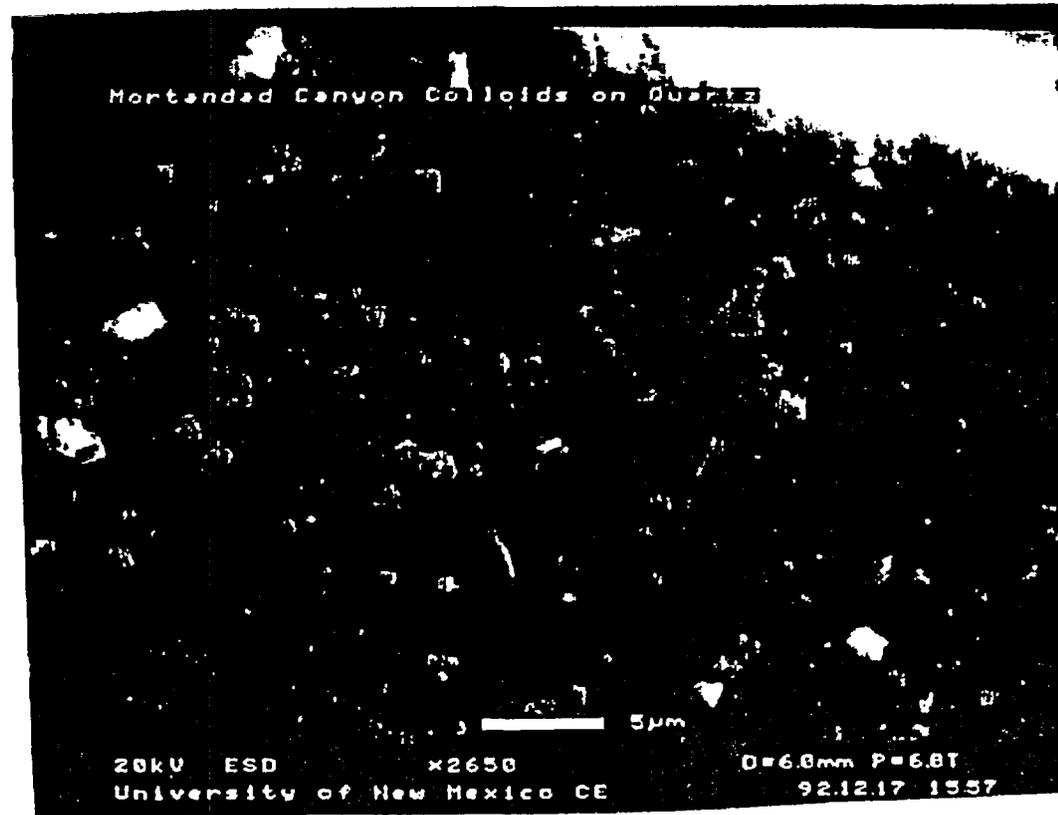
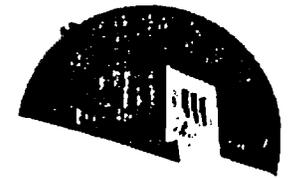
Silica breakthrough curves



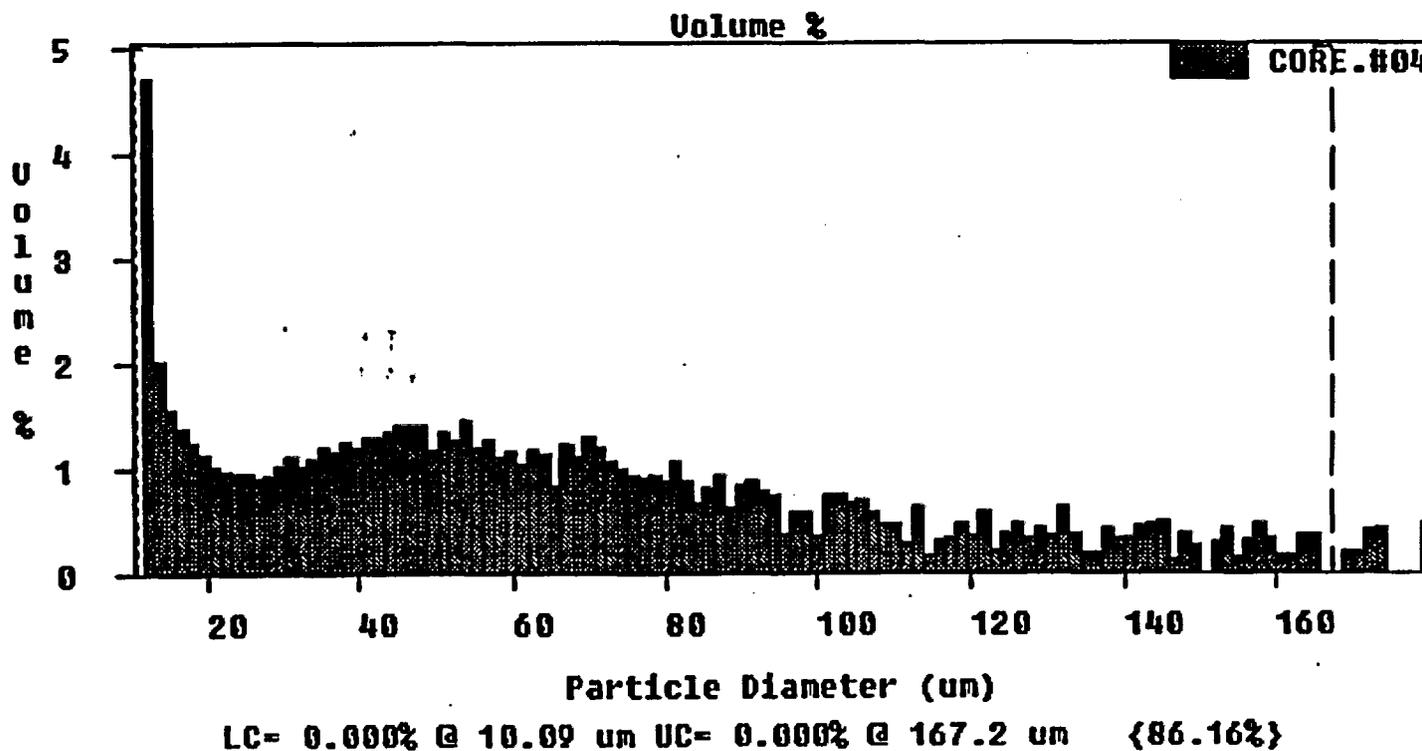
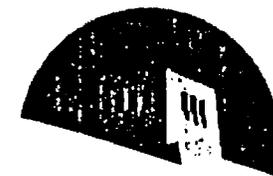
Mortandad breakthrough curves



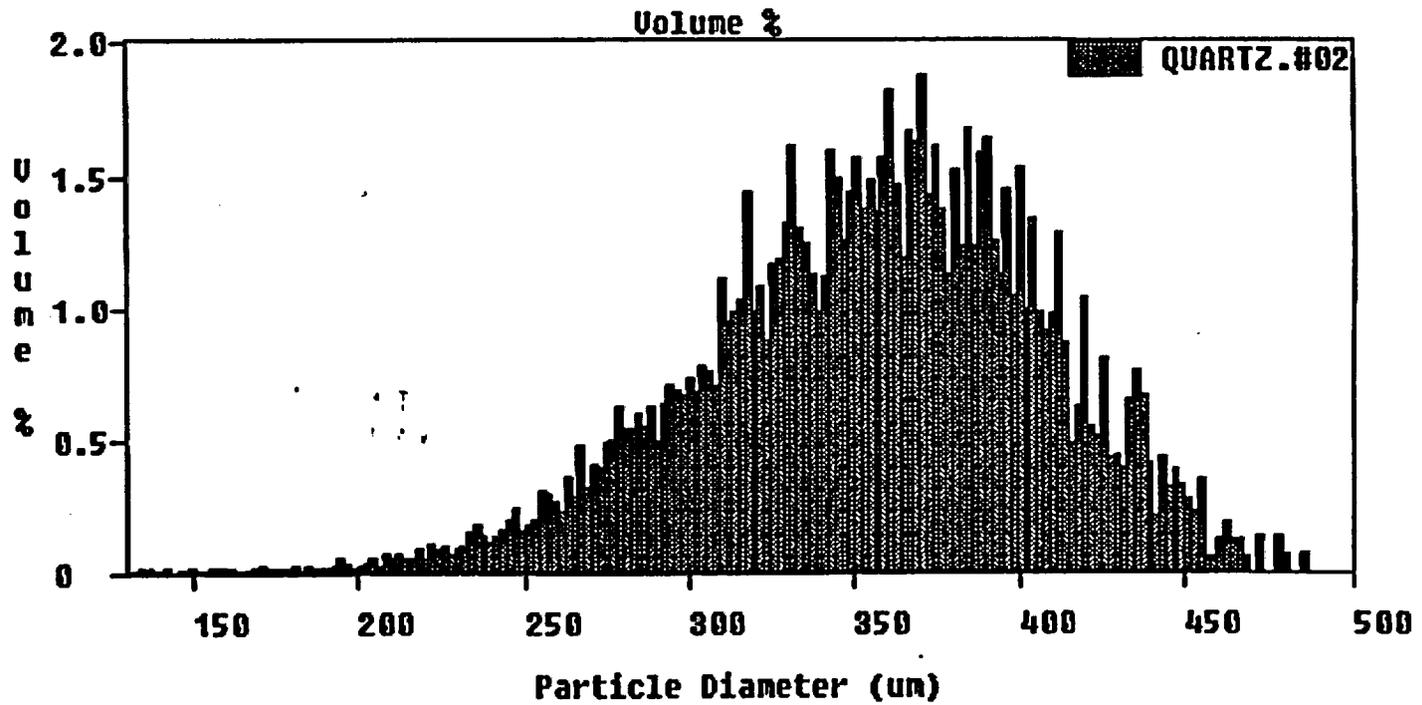
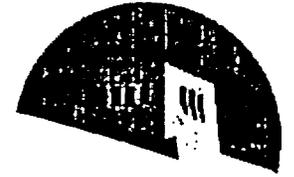
Micrograph of Groundwater Colloids on Quartz



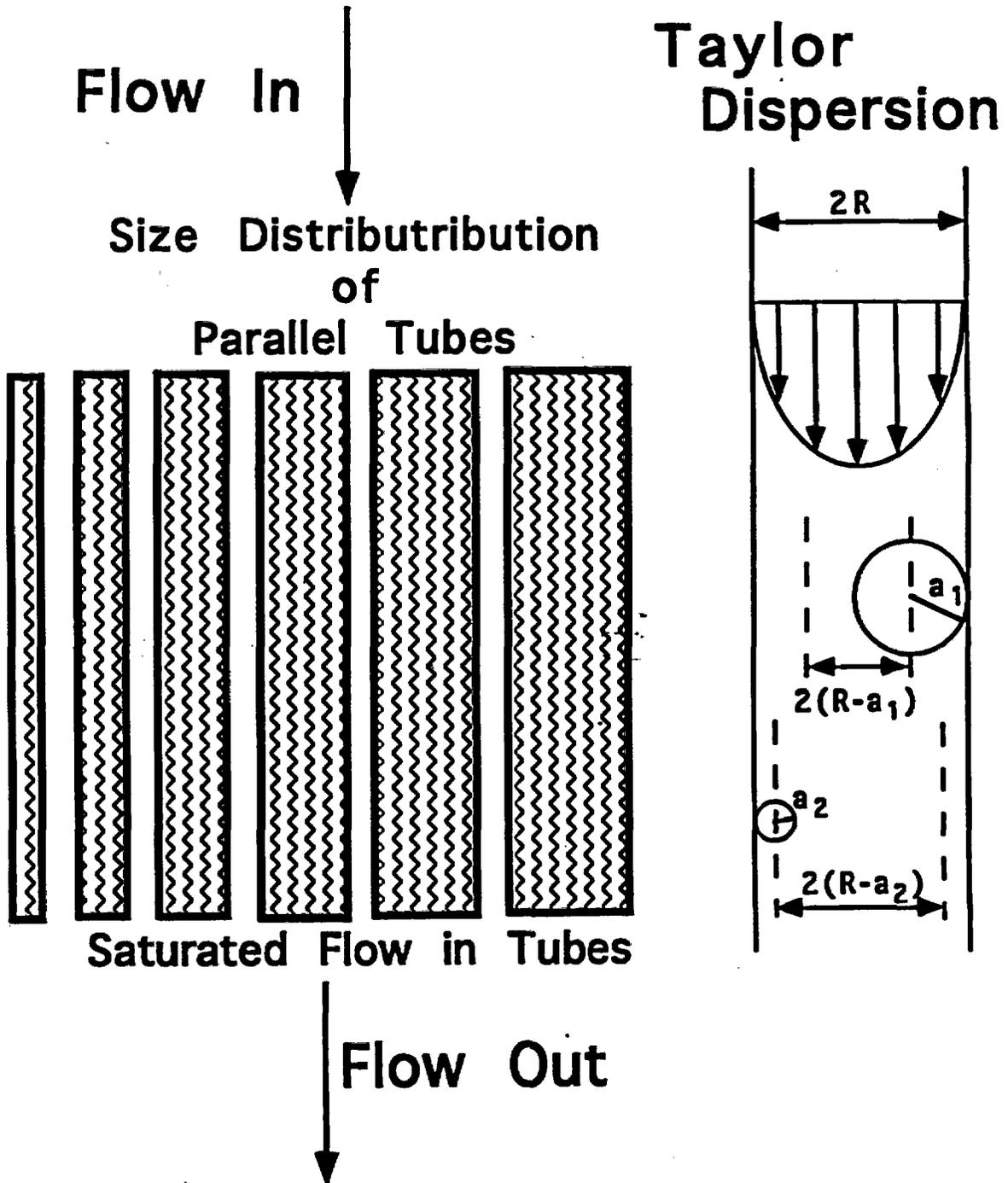
Mortandand Canyon Core Size Distribution



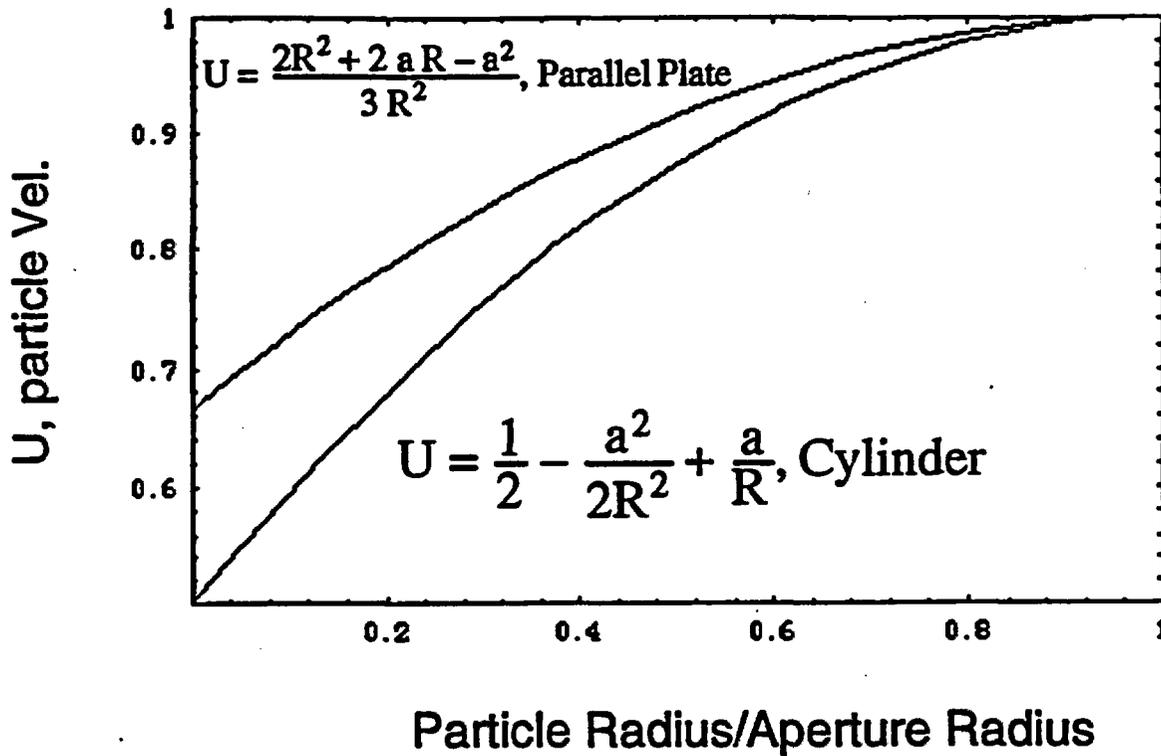
Quartz Packing Size Distribution



Conceptual Model of Unsaturated Flow at YMP



Colloid Velocity in Tubes vs. Parallel Plates



Conclusions:

Limiting Conditions

$$\text{Tubes, } \frac{U_{\text{Particle}}}{U_{\text{Solute}}} = 2.0$$

$$\text{Plates, } \frac{U_{\text{Particle}}}{U_{\text{Solute}}} = 1.5$$

Range of Measured Colloid Concentrations

Site	Conc.	Size(nm)	Composition
Cigar Lake	1-260 mg/L	10-10,000	Clays, oxides, rock particles, organics
Grimsel (crystalline)	10 ¹⁰ part/L; 1 mg/L	70-1000	Silica, clays, Ca silicate, biotite, organics
Nevada	4-60m mg/L	3-200	Clays, quartz
Mortandad Canyon, LANL	250 mg/L	100-2,000	Feldspar, quartz, Clays
YMP, J-13 Olgard	0.027 mg/L	NA	NA

Future Work

YMP-CTCN Calculations

Bounding Calculations:

- YMP-CTCN Colloid Bounding Calculations
- Use USGS hydrology data
 - Unsaturated Zone
 - Welded-Layer 1
 - Vitrophyre-Layer 2
 - Vitric-Layer 3
 - Zeolitic-Layer 3
 - Saturated Zone
 - Fracture Network
- Test various Levels of Colloid Retardation using first order kinetics
- Investigate Parameter Sensitivity