GEOCHEMICAL CONTROLS ON THE COMPOSITION OF SOIL PORE WATERS
BENEATH A MIXED WASTE DISPOSAL SITE IN THE UNSATURATED ZONE

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ABSTRACT

Soil pore waters are collected routinely to monitor a thick unsaturated zone that separates a mixed waste disposal site containing transuranic and low-level radioactive wastes from the Snake River Plain aquifer. The chemistry of the soil pore waters has been studied to evaluate the possible control on the water composition by mineral equilibria and determine the extent, if any, of migration of radionuclides from the disposal site. Geochemical codes were used to perform speciation calculations for the waters. The results of speciation calculations suggest that the installation of the lysimeters affects the observed silica contents of the soil pore waters. The results also establish those chemical parameters that are controlled by secondary mineral precipitation.

INTRODUCTION

In recent years, subsurface contamination by wastes associated with energy-related activities has become an issue of environmental concern. Past waste disposal practices for the isolation of mixed radioactive and hazardous wastes have included placing waste in temporary or permanent subsurface burial sites. At such sites, environmental monitoring for evidence of radionuclide or hazardous material migration is conducted to provide information on long-term effects of waste disposal. One of the purposes of any environmental monitoring program is to determine when corrective action may be required.

Environmental monitoring associated with waste disposal sites located in thick unsaturated zones takes the form of acquiring information on soil moisture content and potential, soil salinity, soil temperature, and soil pore water sampling. Knowledge of the soil moisture conditions and the chemistry of the soil pore water is used to establish the potential pathways for contaminant migration and to determine if subsurface contamination has occurred.

This paper presents an evaluation of soil pore water chemistry used to monitor the potential migration of contaminants from a mixed waste disposal site located over a 177 meter thick vadose zone at the U.S. Department of Energy's Idaho National Engineering Laboratory (INEL) in southeastern Idaho. Ongoing site characterization has demonstrated that chlorinated solvents and transuranic radionuclides have migrated from the disposal area. Environmental monitoring of soil pore water chemistry has been conducted for several years and available data have been used in conjunction with geochemical models to characterize the chemical interactions in the subsurface at the disposal site.

The paper includes a brief description of the site hydrogeology and the instrumentation of the monitoring network. The chemical data collected as part of environmental monitoring are evaluated and a geochemical model is applied to selected analyses. The paper reports results of speciation calculations and discusses possible geochemical controls on the soil pore water and its implications for radionuclide migration.

HYDROGEOLOGIC BACKGROUND

As part of past waste disposal practices at the INEL, transuranic and low-level radioactive mixed wastes have been stored in the Subsurface Disposal Area (SDA) of the Radioactive Waste Management Complex at the INEL in southeastern Idaho. The INEL is located in a shallow basin in the north-central part of the eastern Snake River Plain and overlies the Snake River Plain aquifer (Figure 1).

The unsaturated zone separating the Snake River Plain aquifer from the SDA disposal site is approximately 177 meters thick. The unsaturated zone consists of surficial sediments overlying a complex sequence of thin Pleistocene basalt flows, volcanic breccia zones, and sedimentary interbeds. Basalts constitute approximately 95% of the unsaturated zone.

The subsurface geology of the unsaturated zone at the INEL and the SDA is well-characterized as a result of data collected by the United States Geological Survey and site contractors from numerous monitoring wells on the INEL site. The SDA is located in several meters of surficial sediments. Beneath the SDA, basalt flows range in thickness from 2 to 20 meters, with an...
average thickness of approximately 8 meters. The flows are interlayered with unconsolidated cinders, volcanic breccia, and aeolian, fluvial, and lacustrine sediments. Two major interbeds occur beneath the SDA, at depths of 34 meters (110 ft) and 73 meters (240 ft).4

Hydrology of the unsaturated zone at the INEL is controlled in part by the average precipitation. Precipitation on the INEL site is in the range of 13-36 cm per year, with an average of 20 cm per year.5 Snowfall accounts for 30% of the annual precipitation. In areas of thick alluvial fill, evapotranspiration exceeds 95% of the precipitation.5

\textbf{VADOSE ZONE MONITORING AT THE SDA}

The SDA consists of trenches and pits, some of which were originally excavated down to basalt. A sediment buffer that ranged from 0.67 to 1 meter thick was left between the waste and the uppermost basalt flow. Between 1952 and 1970, approximately 96,300 cubic meters of transuranic and low-level radioactive wastes were emplaced on the sediment buffer and covered with a soil cap. Further burial of transuranic waste was prohibited by regulation in 1970, but disposal of low-level waste has continued until present.

Surface and subsurface environmental monitoring for radionuclides at the SDA has been conducted since the 1960s. An ongoing study to determine the extent of radionuclide migration from the SDA has resulted in the installation of an extensive network of instrumentation to characterize the unsaturated zone. As part of the study, soil pore waters from surficial sediments and sedimentary interbeds in the unsaturated zone have been sampled.

Selection of Sampling Technique

For monitoring soil pore waters in the unsaturated zone, samples are obtained either by extraction of water from a soil sample or by in-situ collection. In-situ techniques have been used at the SDA to provide a long-term monitoring network. Pressure-vacuum lysimeters equipped with porous ceramic cups were selected as the preferred methodology for soil pore water collection, after evaluation of the advantages and disadvantages of the technology, as described below.

Pressure-vacuum lysimeters operate by creating a vacuum within the sampling vessel that causes soil pore water to move under tension into the vessel. The water collected in the sampling vessel is removed using suction or is pushed out by application of nitrogen gas pressure. The chemistry of the sample can be affected by the nature of the sampling vessel or by the method of retrieving the sample.

Porous ceramic cups and polytetrafluorethylene (PTFE) cups were initially tested as sampling vessels. The ceramic cup has a pore diameter of 1.2 micrometers that allows water to enter the cup but prohibits air movement through the cup up to a tension of approximately 200 kPa. The PTFE cup was considered and actually used in some of the first lysimeters because of its inert material properties. However, the low air entry value of PTFE (7 kPa) made it impossible to collect soil water samples from the unsaturated zone under study.

The ceramic cup may add, remove or affect chemical constituents of the soil pore water. Numerous studies have been performed on the representativeness of the samples collected by ceramic cup lysimeter and some changes in soil pore water chemistry due to the
sampling process have been observed. Several milligrams/liter of calcium, magnesium and silica along with several micrograms/liter of aluminum and sodium may be leached from the cup during each sampling event. Studies of chemical interactions of samples and cups suggested that cation and anion chemistry in solutions with concentrations of total dissolved solids (TDS) in excess of 500 mg/l are not changed but trace metal concentrations could be significantly altered. One recent study also indicated that sample pH is not measurably affected by CO₂ degassing during sampling.

The pressure-vacuum lysimeter collects the water from soil pores within an area of influence that depends upon the soil moisture characteristics of the materials surrounding the porous cup, the existing moisture content, the differential pressure between the cup and the media being sampled, and the volume of sample removed. As water is removed from the soil surrounding the lysimeter, water flow lines around the lysimeter are distorted. As a greater volume of water is removed, flow line distortion increases the radius of influence and enables sampling at a greater distance from the cup.

Materials added during installation may also affect the chemistry of the samples. Silica flour is packed around the porous ceramic cup to form the hydraulic connection with the formation. Bentonite is placed above the lysimeter, to seal the sampling zone from water infiltrating down the area disturbed by the borehole, and native materials are used as backfill in the completion of the lysimeter installation. Ion exchange between these materials and the soil pore water cannot be ruled out.

Schematic of SDA Lysimeter Locations

![Diagram of SDA Lysimeter Locations]

Figure 2. Location of lysimeter network at the Subsurface Disposal Area of the Radioactive Waste Management Complex. Triangles show locations of shallow boreholes containing lysimeters. Data used in this study came from waters collected from the numbered boreholes.
The area of influence from lysimeter sampling at this site is assumed to be similar to that described by Peters and Healy.7

GEOCHEMISTRY OF SOIL PORE WATERS

Understanding the chemistry of soil pore waters is a particularly important part of monitoring and characterizing a waste site. The solubility equilibria that control precipitation and dissolution of soil minerals also determine the concentration of major solutes in the waters. The concentration of solutes in the soil pore water will affect the dissolution of radionuclides from the disposed waste and their subsequent migration. Solubility-limiting phases also influence radionuclide migration through removal of dissolved radionuclides from soil pore water by precipitation or sorption.

Water quality data collected from the lysimeter network at the SDA over four years have been studied to better characterize the potential for radionuclide migration. Soil pore water pH, temperature, specific conductance, and dissolved oxygen concentrations were determined in the field. Soil pore waters collected from the lysimeters were analyzed for a suite of inorganic cations and anions. Periodically, waters were collected for radiochemical analyses to monitor any radionuclide migration.8,9

Water chemistry data used in this study were limited to analyses of waters from lysimeters listed in Table 1, because the waters showed low bromide concentrations, and represented the most complete suites of analyses available. The waters were analyzed for Na+, K+, Ca++, Mg++, SiO2, Al++, total iron, HCO3-, SO4-, Cl-, F-, and a suite of trace metals.8,9

Concentrations of total dissolved solids and most major elements appear to reach a steady-state after approximately one year in shallow boreholes, but may take longer to equilibrate in deeper boreholes. The evolution of potassium concentration in the soil pore water with time for shallow and deep boreholes is shown in Figures 3 and 4 as an example of this phenomenon. Similar trends were exhibited by calcium, magnesium, and sodium.

<table>
<thead>
<tr>
<th>TABLE 1. Location of Lysimeters Used in Current Study</th>
<th>Depth of Emplacement (m) (Date of Installation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Borehole</td>
<td>Lysimeter</td>
</tr>
<tr>
<td>C01</td>
<td>L19</td>
</tr>
<tr>
<td>Control borehole</td>
<td></td>
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<td></td>
<td>L20</td>
</tr>
<tr>
<td>D06</td>
<td>DL02</td>
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<tr>
<td>PA02</td>
<td>L16</td>
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</tbody>
</table>

Figure 3. Variation of potassium concentration with time for deep lysimeters. DL06 is a lysimeter in the deep control borehole.

Figure 4. Variation of potassium concentration with time for shallow boreholes. Note the approach to steady-state concentrations after approximately one year. L19 is a lysimeter in the shallow control borehole.
Silica concentrations reached apparent steady-state concentrations soon after lysimeter installation. Waters from control wells, from shallow boreholes, and from deep boreholes have average silica concentrations that range between 70-85 mg/L. Data for the variation of silica concentration with time in shallow boreholes are shown in Figure 5.

Trilinear Piper plots of the concentrations of Na⁺, K⁺, Ca²⁺, Mg²⁺, HCO₃⁻, Cl⁻, and SO₄²⁻ indicate the existence of sulfate waters in the shallow control well, as shown in Figure 6. Lysimeters in shallow boreholes within the surficial sediments produced either bicarbonate or chloride waters, while lysimeters in the deep boreholes produced chloride waters.

Inorganic speciation calculations were conducted to evaluate the effect of geochemical interactions between soil water and geologic media. An equilibrium geochemical code, PHREEQE¹⁰, was used to formulate the ion-association model assumed for the soil pore waters. The thermochemical database used with the code was adapted by the University of Colorado from the MINTEQ code.¹¹ Chemical analyses representative of apparent steady state concentrations were used in calculations. Because field measurements of Eh were not made, the pe of the water was estimated assuming saturation with oxygen in the air in contact with the soil pore waters. Eh values measured with field probes are an ambiguous measure of the oxidation potential of the solution even when available.

Saturation indices (ratio of the ion activity product (IAP) for a given mineral relative to the equilibrium constant for the reaction that forms the mineral (Kₑq)) were computed by the code. It has been demonstrated that variance in the saturation indices increases with the magnitude of the equilibrium constant.¹² An error of 5% of the equilibrium constant has been used previously as a first approximation of the uncertainty in the saturation index.¹² For this study, minerals were assumed to be at saturation if the value of log (IAP/Kₑq) was zero within 5% of the Kₑq value. Minerals were at oversaturation if the log (IAP/Kₑq) exceeded zero by more than 5% of the Kₑq.

Several trends were common to all modeled soil solutions. First, every soil pore water was calculated to be saturated with amorphous silica, and oversaturated with quartz, chalcedony, and cristobalite. Saturation with amorphous silica implies that the formation of colloidal silica is important in these waters. Amorphous silica can form naturally by leaching of quartzose silts and clays that make up the surficial alluvium.

However, in these soil pore waters, saturation with amorphous silica is interpreted to result from the crushed quartz silica flour (grain size less than 40 micrometers) used to install the instruments. The average specific surface area for the silica flour is approximately 3300 cm²/gm, which provide a substantial area for aqueous leaching in the vicinity of the lysimeter. Oversaturation of all solutions with quartz, chalcedony, and cristobalite is interpreted to reflect slow precipitation kinetics. The detrital nature of quartz observed in the surficial alluvium and in the interbeds indicates that secondary quartz growth is not a predominant process.¹³

Regardless of the origin of amorphous silica, if it is present in the subsurface environment, it can serve as a colloidal substrate for radionuclide precipitation or sorption. Advecive transport of any radionuclides associated with natural or man-made colloids is a process that is currently being evaluated.

Waters are either saturated or oversaturated with respect to the calcium carbonates. Soil pore waters from the two lysimeters in the shallow control borehole and the lysimeter in the deep borehole outside the SDA are at saturation with calcite, aragonite, and dolomite. The samples from soils within the SDA are all oversaturated with respect to calcite, aragonite and dolomite. Surficial alluvium contains as much as 40% calcite and sedimentary interbeds at 9 and 34 meters contain approximately 30% calcite.¹³ Aragonite and dolomite have not been observed in the SDA soils or

Figure 5. Variation in silica concentration over time for samples from shallow boreholes.

Figure 6. Piper plot of waters collected in September 1988. The open square represents a sample from the shallow control borehole, C01.
sedimentary interbeds. However, aragonite is not often observed in soil environments because it is either rapidly transformed to calcite or its crystallization is kinetically inhibited. Kinetic controls may also explain why dolomite has not been observed.

In the absence of detectable aluminum in analyses, waters are oversaturated with talc and tremolite rather than smectitic clays. Talc and tremolite are not usually encountered in soil environments, and are interpreted to represent the calcium-magnesian silicate components of phyllosilicates. Smectites are calculated to be undersaturated in these waters, because no aluminum was included in the models since it was below analytical detection in these waters. When the models are formulated with an amount of aluminum equivalent to the detection limit for the analytical method, the waters are calculated to be oversaturated with a wide variety of aluminous phyllosilicates and tectosilicates. Mineralogical and textural evidence supports the diagenetic origin of smectitic clays.

For the few samples in which iron was detected, waters were calculated to be oversaturated with iron oxides, hydroxides, and oxyhydroxides. Iron staining of sediments does occur at the 9,34 and 73m interbeds, and it is likely that there are detectable iron oxides in the surficial sediments as well. X-ray diffraction analysis of poorly crystalline or amorphous iron hydroxides or oxyhydroxides is difficult and it is possible that previous mineralogical analyses of surficial sediments overlooked the presence of the hydrous iron phase(s).

The iron hydroxide minerals have been demonstrated to have a role in the sorption of radionuclides. If the iron minerals have nucleated and grown within the sediments, then they will act to retard radionuclide migration and slow the spread of contamination. However, if the iron hydroxides and oxyhydroxides form colloids in the soil pore waters, they may provide sorption sites for radionuclides and allow the radionuclides to migrate as conservative tracers, without further interaction in the subsurface.

Consideration of the sampling techniques allows an evaluation of the role of iron minerals at this site. "Dissolved" iron detected in selected samples can actually signal the incorporation of particulates, because the iron hydroxides and oxyhydroxides are sparingly soluble. Because field filtration of samples was not conducted early in the operation of the lysimeter network, the possibility exists that colloidal iron in the water was incorporated in the samples and analyzed as a "dissolved species". The potential for colloidal transport of radionuclides cannot be dismissed at this time.

CONCLUSIONS

While the speciation calculations are part of an ongoing effort to understand radionuclide migration at a waste site located in the unsaturated zone, the following conclusions can be drawn:

1. In contrast to conclusions of previous studies, the use of silica flour as a medium around the soil lysimeters has affected the chemistry of the soil pore waters. The interference by artificially introduced silica makes it difficult to determine the possible role of natural amorphous silica colloids in transporting radionuclides.

2. Dissolved bicarbonate concentrations are sufficient to cause precipitation of calcium carbonates. The concentrations of bicarbonate are such that the possible complexation of radionuclides by bicarbonate and oxycarbonate ions is being evaluated as part of the ongoing determination of radionuclide speciation and solubility in the SDA geochemical environment.

3. Calculated saturation indices for iron oxides, hydroxides, and oxyhydroxides indicate that ferric iron phases with high sorptive properties for radionuclides will form. If the minerals are precipitated diagenetically, the geochemical environment in the surficial sediments and the sedimentary interbeds is likely to contribute to significant retardation of radionuclides that may be released from the SDA. Iron hydroxides move as colloids with infiltrating soil pore water, they may contribute to radionuclide transport.

Ongoing environmental monitoring of the site and geochemical studies of radionuclide migration are aimed at establishing the predominant mode(s) of radionuclide transport in the SDA subsurface, and will enable resolution of many of the considerations raised by this study.

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REFERENCES


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