

CHEMICAL EVOLUTION OF LEAKED HIGH-LEVEL LIQUID WASTES IN
HANFORD SOILS

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ABSTRACT

A number of Hanford tanks have leaked high level radioactive wastes (HLW) into the surrounding unconsolidated sediments. The disequilibrium between atmospheric CO₂ or silica-rich soils and the highly caustic (pH > 13) fluids is a driving force for numerous reactions. Hazardous dissolved components such as ¹³³Cs, ⁷⁹Se, ⁹⁹Tc may be adsorbed or sequestered by alteration phases, or released in the vadose zone for further transport by surface water. Additionally, it is likely that precipitation and alteration reactions will change the soil permeability and consequently the fluid flow path in the sediments. In order to ascertain the location and mobility/immobility of the radionuclides from leaked solutions within the vadose zone, we are currently studying the chemical reactions between: 1) tank simulant solutions and Hanford soil fill minerals; and 2) tank simulant solutions and CO₂.

We are investigating soil-solution reactions at: 1) elevated temperatures (60 - 200 °C) to simulate reactions which occur immediately adjacent a radiogenically heated tank; and 2) ambient temperature (25 °C) to simulate reactions which take place further from the tanks. Our studies show that reactions at elevated temperature result in dissolution of silicate minerals and precipitation of zeolitic phases. At 25 °C, silicate dissolution is not significant except where smectite clays are involved. However, at this temperature CO₂ uptake by the solution results in precipitation of Al(OH)₃ (bayerite). In these studies, radionuclide analogues (Cs, Se and Re – for Tc) were partially removed from the test solutions both during high-temperature fluid-soil interactions and during room temperature bayerite precipitation. Altered soils would permanently retain a fraction of the Cs but essentially all of the Se and Re would be released once the plume was past and normal groundwater came in contact with the contaminated soil. Bayerite, however, will retain significant amounts of all three radionuclides.

INTRODUCTION

There are approximately 11 million cubic meters of liquid effluent containing radionuclides stored in large underground tanks at Hanford, Washington [1, 2]. In all, sixty seven tanks are suspected leakers and there are a great many other contaminant plumes around the sited arising from various sources; surface spills, pumping problems, early waste disposal practices, etc.[1] Near the highest temperature tanks (up to 270 °C, with many tanks having been above 100 °C for prolonged periods, [7]) the strongly basic concentrated, aluminum, phosphate and sodium-rich waste solutions[3-6] in contact with silica-rich soil minerals provide an ideal recipe for the in-situ formation of zeolites. Additionally, as cooled fluids flow away from the tanks their pH will fall as they encounter CO₂. This will initiate precipitation of hydrous Al – hydroxides. The predicted location for these reactions are shown in figure 1 (adapted from Appendix H of the GW/VZ Integration Project Specification DOE, 1998). [8]

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Highly soluble radionuclides likely to travel in contaminant plumes include ^{79}Se , ^{99}Tc and ^{133}Cs . The upper limits of the radionuclides in the solutions are approximately 5.7 ppm ^{133}Cs , 20 ppm ^{99}Tc , and up to 70 ppm ^{79}Se . [9] The phases which form as a result of solution interactions with neutralizing media such as CO_2 or silicates must be identified in order to determine the location, speciation and phase association of these contaminants within the Vadose zone. Further, changes in soil permeability as a result of alteration and precipitation processes must be assessed with regard to their impact on the flow paths of past or future leaks. These questions were addressed by initiating a suite of scoping studies intended to simulate the various changes that would occur as a leaked fluid would (DSSF-7) migrated through the vadose zone toward the water table.

EXPERIMENT

Soil-Solution Reactions

Soils used in this study were obtained from the Hanford Reservation and are typical of the sandy surface cover deposited by the last great Lake Missoula flood. The fluid used in these experiments ("DSSF-7") was developed to be similar to that originating from rinsing operations associated with tank 101AW [3]. The major components of the DSSF-7 simulant solution, the radionuclide analogues, and the concentrations of these species are compiled in Table I. The nonradioactive analogues include Re for ^{99}Tc , and nonradioactive Cs and Se for ^{133}Cs and ^{79}Se , respectively. The soils were exposed to DSSF-7 solutions for 1 - 2 weeks at 90° and 200°C in Parr reaction vessels and for 82 days at room temperature, 60° , and 90°C in polyethylene bottles. After completing the 90° and 200°C experiments the liquid phase was isolated from the solid phase by filtration. Concentrations of Cs, Se and Re in both the solid phases and liquid phases were determined by ICP-Mass Spectrometry. The 82 day experimental fluids did not contain radionuclide surrogates but were used to identify solid alteration products and observe textural features resulting from the treatment (i.e. grain cementation and zeolite morphologies).

CO_2 -Solution Reactions

Two experiments were also performed to study uptake of CO_2 by the DSSF-7 test solution. First, an aliquot of DSSF-7 solution was left stirring at room temperature in contact with the air to verify that eventually even this dilute source of CO_2 could neutralize enough hydroxide to initiate precipitation of a solid phase. Second, an accelerated experiment was executed by bubbling pure CO_2 gas through DSSF-7 solution at room temperature. There was enough of this second precipitate that it could be isolated by filtration and analyzed by X-ray diffraction (phase identification) and ICP-MS (radionuclide surrogate content). The remaining DSSF-7 solution was also analyzed by ICP-Mass Spectrometry for Se, Cs and Re.

Table I. Composition of DSSF-7 Simulant Solution

| Component | Concentration in solution | Component | Concentration in solution |
|---------------------------------|------------------------------|--|------------------------------|
| *Cs | 100 ppm | Na ₂ HPO ₃ ·7H ₂ O | 0.014 mol/L |
| *Se | 100 ppm | NaOH | 3.885 mol/L |
| *Re | 100 ppm | Al(NO ₃) ₃ ·9H ₂ O | 0.721 mol/L |
| NaNO ₃ | 1.162 mol/L | Na ₂ CO ₃ | 0.147 mol/L |
| KNO ₃ | 0.196 mol/L | NaCl | 0.102 mol/L |
| KOH | 0.749 mol/L | NaNO ₂ | 1.512 mol/L |
| Na ₂ SO ₄ | 0.008 mol/L | | |

* Radionuclide analogue

RESULTS

Solution-Soil Reactions

Figure 2 shows the X-ray diffraction spectra of unaltered sandy Hanford soil (a), and Hanford soils exposed to DSSF-7 solution for 82 days at 25 °C (b), 60 °C (c) and 90 °C (d). The major phases of the unaltered soils are quartz, plagioclase feldspar and grains of basalt – consisting mainly of feldspar and minor amounts of pyroxene. X-ray diffraction analyses of the soil minerals show that with increasing temperature more of the sample is altered to a cancrinite-group zeolite. At 90 °C both quartz and feldspar were completely removed from the sample. Basaltic fragments, however, were relatively less effected by the treatment. The unaltered soil (consisting of quartz feldspar and basalt grains[10]) and soil altered by DSSF-7 solution at 90 °C are compared by SEM in figure 3. The unaltered soil consists of large, angular grains varying in diameter from several microns to several hundred microns. The altered soil still shows outlines of the original grains, but multiple grains are cemented together by cancrinite overgrowths. The cancrinite overgrowth consists of botryoidal masses (several microns in diameter). Soil alteration as a function of the solution: soil ratio was also studied. At 200 °C, 1 gram of soil and 10 grams of DSSF-7 solution resulted in complete alteration to cancrinite. On the other hand, 8 grams of soil and 10 grams of solution at 200 °C resulted in incomplete alteration of the minerals and quartz was still the dominant phase observed in the X-ray diffraction. In addition, a different well-formed zeolite was were observed in this sample (figure 4). This phase was tentatively identified as analcime by the crystal morphology and by several minor peaks observed in the X-ray powder diffraction pattern, .

Solution-CO₂ Reactions

The precipitate formed from bubbling CO₂ through DSSF-7 solution was identified as bayerite, Al(OH)₃, by X-ray diffraction. A white precipitate, presumably bayerite, was also noted in the experiment exposing DSSF-7 to air. This suggests the CO₂ in the atmosphere is present in sufficient quantity for Al(OH)₃ precipitation from a leaked tank fluid.

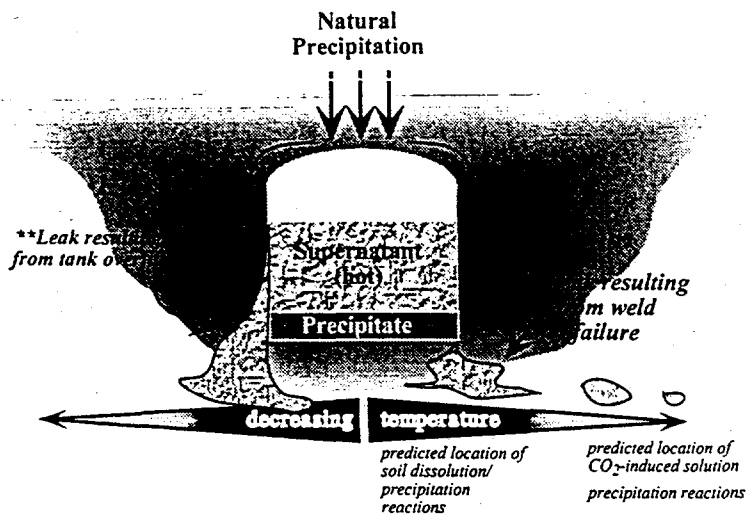


Figure 1. Schematic of a Hanford waste tank, depicting the site of the soil/solution reactions within the Vadose zone.

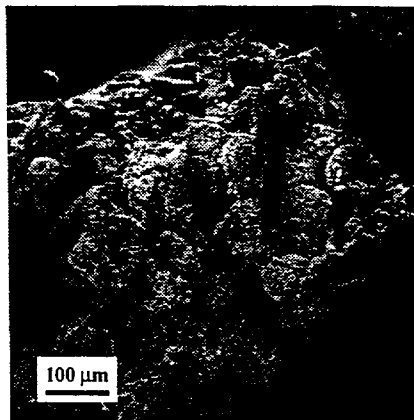
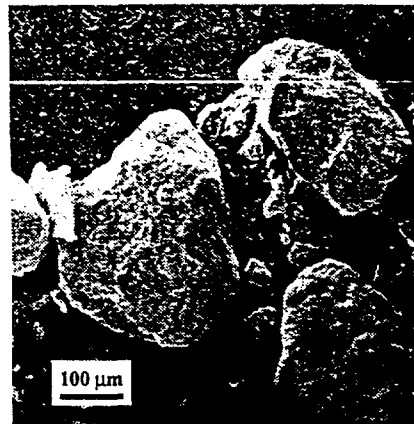


Figure 3. Unaltered Hanford soils; predominantly quartz and feldspar grains (top) Hanford soils altered by DSSF-7 solution at 90 °C; feldspar and quartz grains are overgrown and cemented with cancrinite (bottom). Magnification = 50 x.

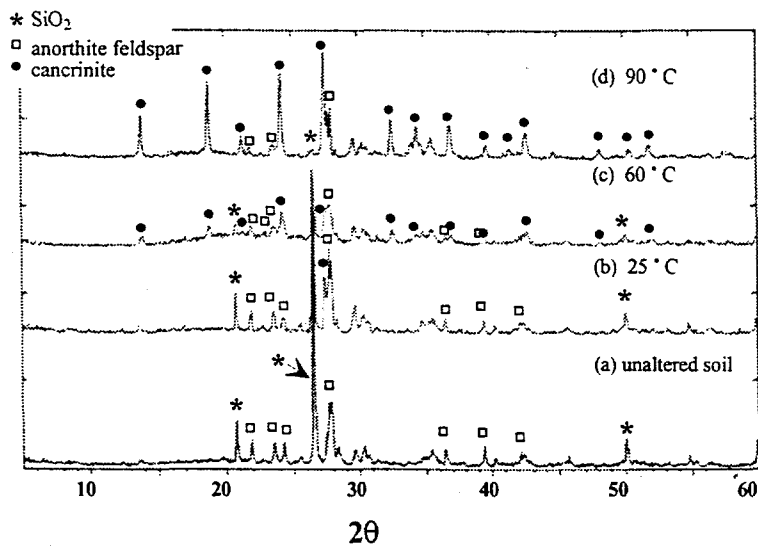
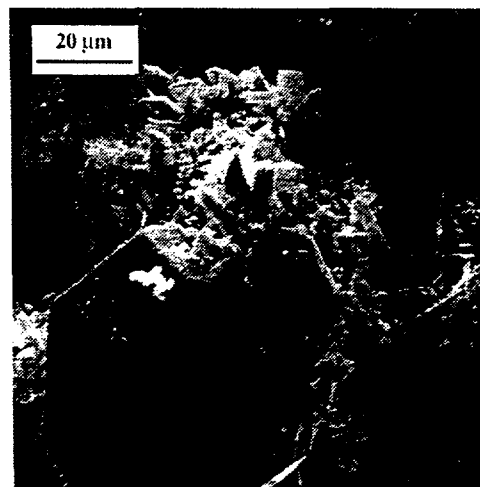


Figure 2. X-ray diffraction spectra of unaltered Hanford soil (a), and soil soaked in DSSF-7 solution for 2 weeks at 25 °C (b), 60 °C (c) and 90 °C (d).

Figure 4. Analcime grown on Hanford soils from DSSF-7 solution at 200 °C



Radionuclide Analogue Sequestration

Se, Cs, and Re concentrations were monitored in experiments of DSSF-7 with both Hanford soils and CO₂ to determine the radionuclide sequestration ability of the reaction products (results compiled in Table II). Major alteration phases identified by X-ray diffraction are cancrinite and analcime (both aluminosilicate zeolites) for the soil-solution experiments, and Al(OH)₃ for the CO₂ precipitation experiments. The zeolites are capable of sequestering Cs⁺ in micropores, and Al(OH)₃ may sandwich Cs⁺ between octahedral layers. The Se and Re, which exist in solution primarily as SeO₄²⁻ and ReO₄⁻, may coprecipitate or surface adsorb onto alteration phases.[11-14]

In general, a 10 - 20% decrease in concentration of the radionuclide analogues was observed in the reaction supernates. Higher soil : solution ratios resulted in removal of more of the radionuclide analogue from solution. There is a noticeable decrease in Cs concentration from the solution of experiment 5, as well as the relatively high concentration of Cs in the reacted solids (Table II, values in parenthesis). This is the only experiment in which analcime was identified as an alteration product. This suggests that the selectivity for Cs is greater for analcime than for cancrinite.

Further, both Re and Se were removed from the fluid during the sediment - DSSF-7 interaction studies, but were not detectable in the reacted sediments. This suggests that the process responsible for their removal could be reversed by exposing contaminated sediments to fresh groundwater once a plume had passes. It also follows that neither anion seems to have followed the more abundant nitrate, nitrite, and carbonate into the anion sites present in the cancrinite structure. Part of the Cs, however, was retained after the sample was washed which suggests it is fixed in the zeolitic alteration products. Finally, the ability of the bayerite to retain all three radionuclide is notable. Thus, such precipitates may significantly impact radionuclide mobility in the cooler, more distant, parts of the vadose zone.

Table II. Radionuclide Analogue Concentration in Experiment Supernates

| Experiment Description | PPM of radionuclide analogue in experiment supernate and in the solid reaction products () | | |
|---|---|------------|------------|
| | Se (ppm) | Cs (ppm) | Re (ppm) |
| 1) DSSF solution initial concentration | 86 | 96 | 98 |
| 2) 1:10 soil : solution 90 °C / 2 weeks | 76 (>250) | 74 (49) | 89 (>5) |
| 3) 1:1 soil : solution 90 °C / 2 weeks | 72 (>250) | 63 (38) | 81 (>5) |
| 4) 1:10 soil : solution 200 °C / 1 week | 79 (>250) | 87 (30) | 88 (>5) |
| 5) 1:1 soil : solution 200 °C / 1 week | 71 (>250) | 39 (124) | 84 (>5) |
| 6) CO ₂ enhanced Al(OH) ₃ precipitation | 68 (8,390) | 78 (9,000) | 84 (8,020) |

CONCLUSIONS

Studies have been carried out in order to: 1) model the reactions which take place between a hot alkaline tank solution and soil fill adjacent to a leaking tank at Hanford, and 2) predict the fate of ^{133}Cs , ^{99}Tc , and ^{79}Se radionuclides. Preliminary results reveal that at high temperatures the sediments will be zeolitized and at lower temperatures precipitation of bayerite (or related hydrous Al oxides) may dominate. These studies have also shown that, at least in a batch reactor mode, the radionuclides are only partially immobilized by these changes. Better simulations involving more appropriate mass:fluid ratios and a realistic assessment of mass transport processes are necessary before these results could be applied to quantitatively predicting radionuclide distributions in an actual field setting.

Secondly, the overgrowth textures, cementation of grains, and voluminous precipitation of hydrous Al-hydroxide gels all suggest that chemical reactions within a migrating plume will almost certainly alter fluid flow paths adjacent to a leaking tank. This result must be considered when developing vadose zone hydrologic models to predict the transport of radionuclides away from a leaking tank.

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