

Sorption and transport behavior of radioactive iodine

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1. Introduction

Nuclear wastes, which leaked from single-shell underground storage tanks or from pipelines entering/exiting the tanks at the U.S. Department of Energy (DOE) Hanford Site, have been detected in the subsurface since the 1950s. Radionuclides present in the Hanford tanks include uranium and transuranic elements, such as neptunium, plutonium, and americium, as well as radioactive and stable isotopes of lighter elements resulting from fission and activation processes [1]. The U.S. Department of Energy's current plan is to retrieve the waste currently stored in the tanks and to separate it into a high-activity fraction (having relatively little volume but most of the radioactivity) and a low-level activity fraction (having most of the volume but less radioactivity). The high-activity fraction will be vitrified and is planned to be disposed at the proposed federal geological waste disposal facility, while the low-activity immobilized fraction will be also vitrified (some may also be immobilized in other processes) and will be disposed in a near-surface Integrated Disposal Facility (IDF) located at the 200 East Area on the Hanford Site [2]. Previous performance assessment (PA) analyses of the proposed IDF site have shown that ^{129}I , ^{237}Np , ^{79}Se , ^{99}Tc , and $^{233,235,238}\text{U}$ pose the most potential risk to human health. Because the severity of environmental problems associated with these radionuclides depends on how readily these contaminants migrate from the source through the accessible environments, the risks associated with relatively mobile radionuclides are a great concern.

Radioactive iodine has been released into soils and the atmosphere during the course of nuclear power plant operations, nuclear weapon tests, nuclear accidents such as that at the Chernobyl power plant, and operations and disposal activities associated with nuclear-fuel reprocessing. Health risks associated with the release of radioactive iodine, especially as ^{129}I , are a significant environmental concern because of the long-half life of ^{129}I ($t_{1/2}=1.6 \times 10^7$ years) and high mobility of all iodine isotopes in subsurface environments. Iodine is known to occur in several oxidation states (Fig. 1). In most aqueous environments, iodine is present in the -1 valence state as the iodide ion, I^- . The stability range of I^- extends almost over the entire pH and Eh range for the thermodynamic stability of water. In marine and highly oxidizing environments such as surface waters

and some highly oxygenated shallow ground waters, iodine may be present in the +5 oxidation state as the iodate ion, IO_3^- . Under highly oxidizing conditions at pH values less than 4, molecular $\text{I}_2^\circ(\text{aq})$ may form from the reduction of IO_3^- or oxidation of I^- .

In this study, macroscopic batch sorption and flow-through column experiments were conducted to increase our understanding of sorption and transport behavior of radioactive iodine using IDF-specific sediments from the second borehole (C3177) and IDF-specific solutions including simulated glass leachate.

2. Methods and Results

The Hanford sediment collected from the IDF site consists of a mixture of gravel, sand, silt, and clay, but sand-sized particles are dominant. After removing gravel particles (>2 mm), the sediment was used in batch sorption and flow-through column experiments. Uncontaminated groundwater collected from well 699-S3-25 at the Hanford Site and simulated glass leachate were used as background electrolytes for two separate suites of batch sorption experiments. The composition of the simulated glass leachate is based on the pore water composition in vadose zone predicted by the STORM model (a fully coupled chemical reaction-transport code) for the low-activity waste glass filled repository at steady state conditions. Batch sorption experiments were conducted with 15-mL polypropylene centrifuge tubes by mixing sediment and either groundwater or simulated glass leachates spiked with radioactive iodine, ^{129}I of known activity (3.7×10^5 Bq/L). After 7 days contact, supernatant solution was separated by centrifugation and passed through 0.45- μm pore size filters. A 1-mL aliquot of filtered supernatant solution was mixed with 15-mL of cocktail solution in a glass scintillation vial and counted by liquid scintillation for ^{129}I .

The flow-through column experiments were conducted using a poly-ether-ether-ketone (PEEK) column (1.91 cm in diameter and 7.62 cm in height). Each end of the individual columns was covered by a small piece of Spectra/Mesh® to avoid the loss of particles during the flow through experiments. To achieve uniform packing, each column was packed with Hanford sediment using a vibrating Vortex-Genie 2 mixer placed on the sidewall of the column while a continuous stream of dry sediment was added. The columns were then saturated with groundwater to establish the desired flow rate and to remove any easily dispersible particles. Constant flow rate was maintained with a syringe pump and upward flow was used to minimize channeling or preferred flow in the columns. Radiotracer (^3H) in deionized water was introduced as a nonreactive conservative tracer to

determine the dispersion coefficient. After obtaining ^3H breakthrough for each column, the ^3H input solution was immediately replaced by groundwater spiked with radioactive iodine, ^{129}I (3.7×10^5 Bq/L). Effluent samples were collected, filtered through 0.45- μm pore size filters, and the radioactivity of each effluent was analyzed by the same methods described for the batch sorption experiments. Breakthrough curves (BTCs) were graphically represented by plotting the relative activity, C/C_0 , for each radionuclide versus pore volumes eluted. The transport parameters were determined by curve fitting of the analytical solution of the advection-dispersion equation to the measured breakthrough curves (BTCs) with the CXTFIT code.

2.1 Tc Eh-pH Diagram Calculation

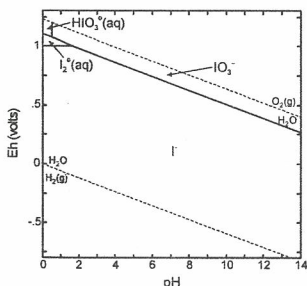


Fig. 1. Eh-pH diagram for dominant iodine species at 25°C for the synthetic groundwater.

2.2 Radioactive Iodine Sorption Results

Radioactive iodide showed low batch K_d values on three Hanford sediments in contact with both solutions, suggesting little interaction of ^{129}I at mineral-water interfaces. Even though a relatively high K_d value for iodide sorption onto illite has been reported [3], iodide sorption on most sorbents including bentonite, hematite, calcite, and montmorillonite has been found to be negligible. Slightly higher K_d values for ^{129}I sorption onto Hanford sediments in contact with Hanford groundwater were observed compared to those determined with simulated glass leachates. The increased sorption from the relatively lower pH groundwater conditions occurred on the pH-dependent protonated surface sorption sites for minerals present in the sediment. The minor changes in measured K_d values for ^{129}I on these three Hanford sediments were considered to result from different mineralogical compositions and specific surface areas. Based on the low average K_d values (0.28 ± 0.12 and 0.09 ± 0.06 under Hanford groundwater (pH 7.8) and simulated glass leachate (pH 9.0), respectively on C3177 borehole sediments, the mobility of ^{129}I is also considered to be rather high in both near and far-field regions at the proposed Hanford Site disposal facility.

2.3 Column Results

Because of the slight sorption affinity of ^{129}I on the Hanford sediment under groundwater condition ($K_d=0.17$ for C3177-110), ^{129}I transport behavior through the same sediment was slightly retarded compared with that of the non-reactive tracer (^3H). Slight retardation of ^{129}I was noticeable in low pore volumes and that long tailing was found in the later stages of the breakthrough. Although a classical equilibrium model showed reasonable fit results ($r^2=0.96$) for the iodide BTC, a non-equilibrium two-region model fit the data better, especially for the measured data at larger pore volumes. In addition, some irreversible ^{129}I sorption on the Hanford sediment was found in our previous work on iodide sorption linearity and reversibility. Higher desorption K_d values for ^{129}I on Hanford sediment, are likely caused by slow desorption processes controlled by diffusion between mobile and immobile regions that leads to the tailing.

3. Conclusions

Both batch sorption and column experiments revealed that ^{129}I was highly mobile on the Hanford sediments under both groundwater and simulated glass leachate conditions at the Hanford Site. The new data, especially for glass leachate solutions, will allow future PA predictions to refine the fate of contaminants in the near-field region of the vadose zone that will be at higher pH conditions than ambient as constituents leach from the glass. Therefore, ^{129}I will remain as the potentially one of the most mobile radioactive contaminants disposed in the proposed IDF.

4. REFERENCES

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