Behavior of Radionuclides and RCRA Elements in Tank Backfill Grouts

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ABSTRACT

One approach to decommissioning emptied high-level waste tanks is to backfill them with grout. Because of the long lives and high toxicity of some of the contaminants, the chemical behavior of the contaminants in the grout need to be understood, especially as the grout ages and weathers over long times. In this paper, the sequestration of technetium and iodine in contact with two grout formulations, and their component materials, is discussed. Preliminary results are presented of experiments examining the solubility of actinides in contact with the grouts as pH is lowered and carbonate content increased, representing conditions of a weathered grout system.

INTRODUCTION

High Level Waste (HLW) vitrification at the West Valley Demonstration Project (WVDP) has been completed and the facilities that managed HLW need to be decommissioned. The disposition of these facilities, including the HLW tanks, is being evaluated in the West Valley Decommissioning Environmental Impact Statement. One of the alternatives being considered in the EIS is in-place closure of the HLW tanks. Under this alternative, the residual waste in the tanks would be stabilized in a grout matrix and an engineered cap and a system of slurry walls would hydraulically isolate the grouted tanks. This paper discusses the results of a testing program conducted at Brookhaven National Laboratory to examine the performance of two different grout formulations and individual grout components to immobilize and retain HLW contaminants.

The objective of the work is to determine to what extent a variety of contaminants, including fission products, actinides, and RCRA elements are sequestered by two grout formulations. The conceptual model for this study is as follows: The waste remaining in the tank contains radionuclides and other contaminants, much of which will adhere to tank walls and internal structures. A large mass of grout is poured into each high-level waste tank to encapsulate the contaminants. Initially the contaminants will be well sequestered, but over thousands of years the process of aging and weathering may lead to cracks allowing rainwater and groundwater to gain access. Ultimately, the grout/waste environment will be an open system. In this condition water will move through the grout, exposing it to O_2 and CO_2 from the air and HCO_3^- from the groundwater. Thus, we are considering an oxidizing environment containing carbonate.

Initially the solubility of many, but not all contaminants, will be constrained by chemistry dominated by the grout, primarily by the high pH. This is controlled and buffered by the portland cement and blast furnace slag components of the grout, which maintain a solution pH of about

12.5. The pH will slowly diminish as $Ca(OH)_2$ and KOH dissolve, are carried away by water, and $CaCO_3$ forms. As these conditions develop, the behavior of some contaminants comes into question. In our conceptual model, although the grout is formulated to provide some reducing capacity in order to be conservative, this mechanism is not considered. In addition to solubility constraints imposed by pH, the various contaminants may be incorporated into a variety of solid phases. Some may be incorporated into newly forming compounds as the grout sets and cures. Others may be the result of slower reactions, but could become important over time as contaminants are exposed to evolving chemistry in the grout. Still other solid phases may form from reactions between contaminants and grout components; not only the cementitious materials, but also the additives used in the grout. Another process that may exert some control on contaminant concentrations is adsorption onto solids within the grout. These may be additives such as the fluorapatite or zeolite that are substantial percentages of the grouts being considered here. They may also be minerals, typically Ca-Al-Si materials that form in the grout system as cement sets. In addition, as the grout weathers over time, $CaCO_3$ minerals, such as calcite and aragonite, will form as a rind on the grout and as a fracture-filling mineral. Some contaminants are likely to be incorporated into these minerals, to a greater or lesser extent, as they precipitate. For some elements, such as U, there is significant literature exploring the incorporation into $CaCO_3$, but for others there is essentially no information.   This is also the case for much of the chemical regime of the grouts. Initial conditions are at pH values around 12 and information is often sparse.

To obtain data on the behavior of a wide range of contaminants that are present in the West Valley Tanks, an experimental program was conducted that explored contaminant sorption/desorption/solubility in the presence of the grout and individual components of the grout under alkaline conditions. As the grout ages and weathers over long times, the pH will decrease. Weathering products (especially calcium carbonate minerals; calcite, aragonite and vaterite) will precipitate, and the chemistry of water in contact with the grout will be altered [1]. The impact of these changing conditions on the fate of contaminants that were initially sequestered, was explored for U, Pu, Am, Cm and Np. Objectives of this work were to:

1) develop adsorption isotherms for 23 elements, including fission and activation products, actinides, and RCRA elements.
2) determine the behavior of actinides as the chemistry of the aging grout system is altered.
3) determine the relationships among pH, water chemistry, and advection of groundwater through the grout as they control the fate of uranium.

In this paper we will concentrate on results of isotherm experiments for two long-lived fission products, I and Tc. In addition, some initial results of experiments with actinides will be discussed.

MATERIALS AND METHODS

Two grout formulations were prepared based on formulae provided by West Valley. For Grout 21, the composition (as wt %) was: 7.6% cement, 32.6% fly ash, 10% zeolite, 12.5% blast furnace slag (BFS), and 37.2% water. For Grout 26, it was 8.9% cement, 42.2 % fly ash, 12.0% apatite, 13.0% blast furnace slag, and 23.9% water. The grout was allowed to cure for 7 days and was then gently crushed so that it passed through a # 20 (< 0.84mm) sieve. The material was stored under high purity nitrogen for future use. Experiments were also conducted on individual

components of the grout under high pH conditions. The contact solution used in the experiments was based on porewater taken from the cement used in the grout. It consisted of 1.20 g /L of $Ca(OH)_2$ and 0.47 g/L of KOH. The solution was filtered through a glass-fiber filter under pressure and stored in a glass stopper bottle. This solution had a pH of 12.3.

The batch isotherm experiments, for partition coefficient (K_d) determinations, contained 2 g of solid and 55 g of contact solution and tracer. They consisted of the two grouts and component materials exposed to the Ca/K OH contact solution. This choice of contact solution was made to simulate the pore-water of the grout as it is controlled by portland cement. Five tracer concentrations in the initial solutions varied by a factor of about 100. These experiments were sampled (5 mL samples filtered through 0.22 µm syringe filters), the pH measured, and analysis performed for the tracer by gamma spectroscopy (for I-125) or liquid scintillation counting (for Tc-99).

Similar experiments were conducted for actinides but were resampled after 500 and 550 days. In addition experiments were conducted in which the pH and carbonate content of the solutions were adjusted to assess solubility of the contaminants under conditions anticipated for the grout system after protracted times.

RESULTS

Iodine Isotherms
Iodine sorption isotherms were developed using I-125 tracers with a specific activity of 10 Ci/g. The grout experiments ran for 31 days, while the grout component experiment ran for 67 days. Little, if any, uptake of iodine occurred on the grouts and concentrations were essentially steady state within a few days. Although uptake was very low, measurable values were obtained. As shown in Fig. 1, the isotherms were linear with slopes for Grouts 21 and 26 of 0.66 and 0.81, respectively. The slope on these plots equates to K_d. In most cases, uptake onto the various components of the grout was low. The exception was sorption onto cement, which was linear with a slope of 210 mL/g. All other materials had slopes (K_d) of less than one. Isotherms for individual components are shown in Fig. 2, and the K_d values from the isotherms are given in Table I.

Hydrated cement paste (HCP) was found by Atkins and Glasser [2] to take up 99% of iodine tracer, while cement containing BFS retained about 85%. They suggest that iodine in cement is in the form of iodide and substitutes for sulfate in ettringite or monosulfate phases that develop as cement sets. Bonhoure et al [3] examined iodide (I^-) and iodate (IO_3^-) uptake by HCP by x-ray absorption spectroscopy. They found that both iodide and iodate were stable in cement systems and did not change on incorporation into cement. In HCP, iodate was apparently present as a free solution. The very low retention on our grouts relative to that of the cement implies that there is significant competition for sorption sites from other anions. Of interest is that the Kd values for the grouts are very similar to that of the fly ash alone and in fact the difference in Kd for the two grouts is proportional to the percentage of fly ash contained in the two grout formulations.
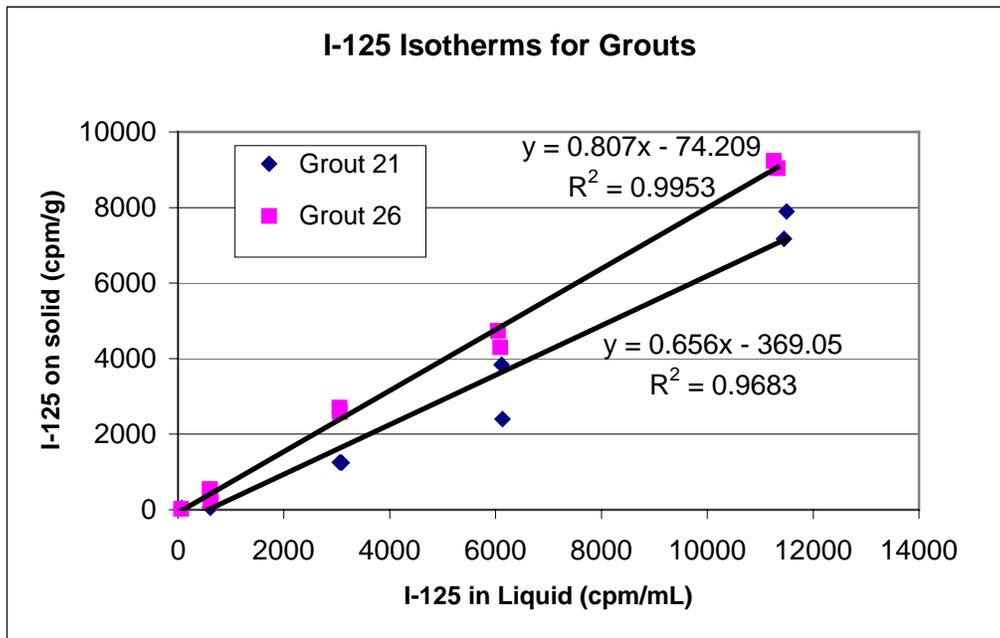
I-125 Isotherms for Grouts

$y = 0.807x - 74.209$
$R^2 = 0.9953$

$y = 0.656x - 369.05$
$R^2 = 0.9683$

Legend: Grout 21, Grout 26

Y-axis: I-125 on solid (cpm/g)
X-axis: I-125 in Liquid (cpm/mL)

Fig. 1. Isotherm for iodine onto grout materials, showing that there was very little uptake of iodine

Iodine Sorption on Grout Components

$y = 209.94x + 14906$
$R^2 = 0.9898$

Legend: Cement, Zeolite, Apatite, Blast Furnace Slag, Fly Ash

Y-axis: I-125 on Solid (cpm/g)
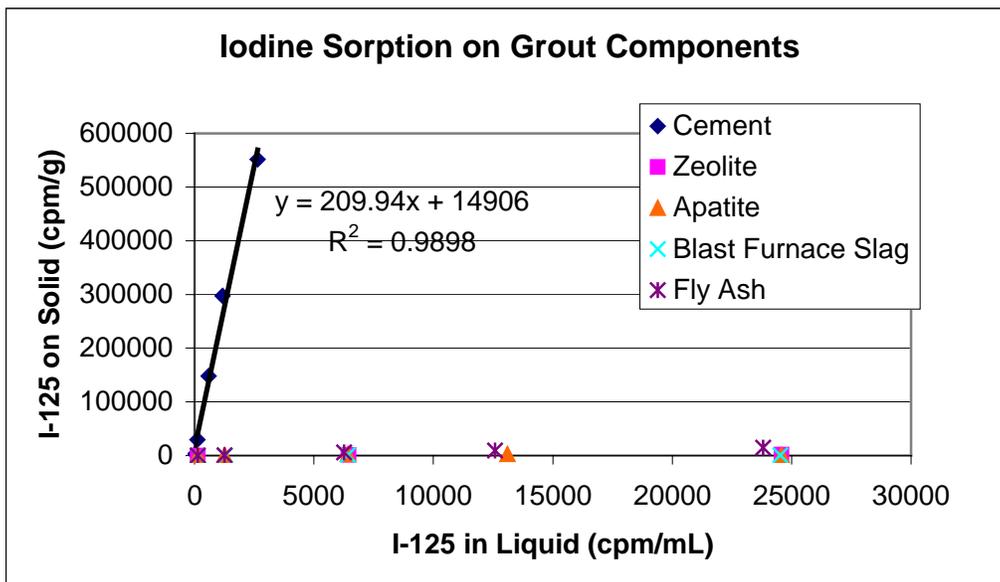X-axis: I-125 in Liquid (cpm/mL)

Fig. 2. Isotherm for iodine sorbed onto grout component materials. Cement provided the greatest uptake of iodine

Table I. K_d Values for I-125

Material	K_d (mL/g)	Material	K_d (mL/g)
Apatite	Nil	Blast furnace slag	Nil
Cement	210	Grout 21	0.66
Fly ash	0.63	Grout 26	0.81
Zeolite	Nil		

Technetium Isotherms

The tracer used was Tc-99, as NH_4TcO_4, with a specific activity of 0.017 Ci/g. Tc was added to the experiments as the pertechnetate ion (TcO_4^-). The grout sorption experiments ran for 43 days, while the component experiments sorbed for 51 days. Concentrations used in the isotherm experiments were: 0.055, 0.027, 0.014, 0.003, and 0.0003 µCi/mL. Uptake of Tc-99 by the two grouts was limited to between 2 and 4 % and reached steady state after about 6 days. There was little difference in uptake of Tc-99 by the two formulations, both with slopes less than 1, as shown in Fig. 3 and Table II. Most of the grout components showed little, if any, capacity to sorb Tc. Blast furnace slag, shown in Fig. 4, had the highest uptake with a K_d of 12 mL/g, followed by cement with a K_d of 2 mL/g.
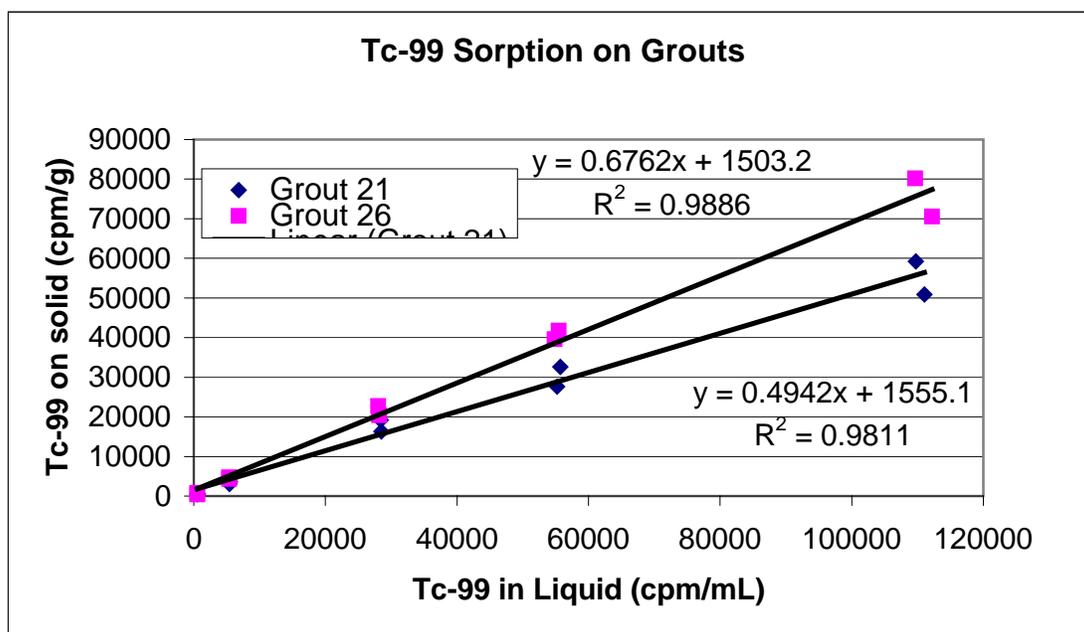

Fig. 3. Isotherms for Tc-99 sorbed on grouts, indicating that little sorption takes place on these materials
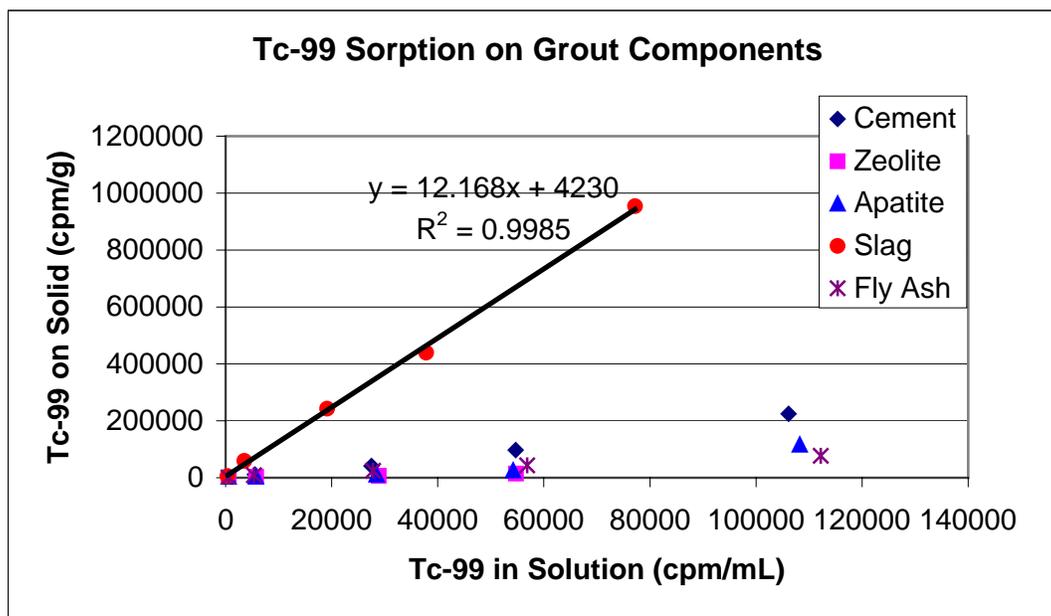
Fig. 4. Isotherm for Tc-99 onto the grout component materials. The slag provided the greatest uptake of Tc

Table II. K_d Values for Tc-99

Material	K_d (mL/g)	Material	K_d (mL/g)
Apatite	1.0	Blast furnace slag	12.2
Cement	2.1	Grout 21	0.5
Fly ash	0.7	Grout 26	0.7
Zeolite	Nil		

Retention of Tc is generally the result of reduction from Tc(VII) to Tc (IV) [4], and this would explain the activity of BFS to sequester some Tc. However, this capacity did not carry over to the grouts. Allen et al. [5] studied the oxidation state of Tc in various cement-based materials by x-ray absorption spectroscopy. They found that BFS reduced only a fraction of the Tc, which is consistent with our isotherm data. Reduced sulfur compounds were much more effective reducing agents for Tc and resulted in bonding of Tc and S[5]. Moreover, they determined that the presence of pulverized fly ash was detrimental to Tc reduction. Given the very long times under consideration, it seems safest not to assume reducing conditions based on activity of the slag component.

Preliminary Results of Batch Tests with Actinides

In contrast to the two fission products discussed above, the actinides partition strongly into grouts. Solution concentrations are primarily controlled by solubility at high pH. A major

concern is the long-term behavior of these elements as the pH of the grouted system slowly is lowered as leaching and reactions remove hydroxides and other components that maintain the high pH. For some elements, such as U, the incursion of carbon dioxide also presents a challenge because it can form readily soluble carbonate complexes. Experiments were conducted that explored the behavior of actinides in contact with the grout (and components of the grout) as the pH was lowered and carbonate content increased.

Am and Cm remained sequestered by the grouts as pH was lowered. Np began to be released around pH 11 and in the presence of the grouts became steady-state around 3×10^{-8} mol/L. This concentration was maintained even as pH decreased to around 8. Some of the individual components of the grout, especially the fly ash, were less able to retain Np as pH decreased and solution concentrations in contact with it were as high as 4×10^{-6} mol/L. In both short-term and long-term (502 days) tests, Pu in contact with the grout was below the detection limit of 3×10^{-11} mol/L, even when pH decreased to 10.1. In another experiment in which carbonate was added, Pu solution concentrations increased as pH decreased below 10.3. Concentrations reached 1.8×10^{-9} mol/L by pH 9.5, in the presence of large concentrations of $KHCO_3$. A set of flow through column experiments were run with grout spiked with U and simulated West Valley groundwater. These columns ran for 150 days, while pH, U, and other elements were measured in the effluent. The pH declined from 11.8 to 8.2 over about 1000 pore volumes, while retention of U in the grout was 90-93 %.

The information being developed in this program will help define controls on contaminant concentrations in water in contact with grouts. In cases where solution concentrations of contaminants are not acceptable, this work indicates possible approaches to grout formulations that may be more effective. By altering pH and carbonate content and monitoring changes of solution chemistry we hope to better define the long-term behavior of grouts, as they weather and age.

ACKNOWLEDGEMENTS

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