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# PRETREATMENT OF TC-CONTAINING WASTE AND ITS EFFECT ON <sup>99</sup>Tc LEACHING FROM GROUTS

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November 2006

Process Science and Engineering  
Savannah River National Laboratory  
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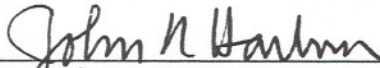
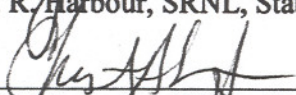

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## REVIEWS AND APPROVALS

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## ABSTRACT

A salt solution (doped with Tc-99), that simulates the salt waste stream to be processed at the Saltstone Production Facility, was immobilized in grout waste forms with and without (1) ground granulated blast furnace slag and (2) pretreatment with iron salts. The degree of immobilization of Tc-99 was measured through monolithic and crushed grout leaching tests. Although Fe (+2) was shown to be effective in reducing Tc-99 to the +4 state, the strong reducing nature of the blast furnace slag present in the grout formulation dominated the reduction of Tc-99 in the cured grouts. An effective diffusion coefficient of  $4.75 \times 10^{-12}$  (Leach Index of 11.4) was measured using the ANSI/ANS-16.1 protocol. The leaching results show that, even in the presence of a concentrated salt solution, blast furnace slag can effectively reduce pertechnetate to the immobile +4 oxidation state. The measured diffusivity was introduced into a flow and transport model (PORFLOW) to calculate the release of Tc-99 from a Saltstone Vault as a function of hydraulic conductivity of the matrix.

## INTRODUCTION

Previous work between Savannah River National Laboratory and Sandia National Laboratory demonstrated that ground granulated blast furnace slag (BFS), as part of the cementitious component of a grout formulation, can reduce and immobilize pertechnetate to Tc (+4) either in water or a dilute salt solution [1]. The grout formulation used in that work has been proposed as the reducing grout for Hanford Tank Closure.

The Saltstone Production Facility at Savannah River will treat a waste stream with higher salt concentrations ( $[\text{Na}^+]$  of ~2 to 6 M). It is therefore important to determine whether Tc-99 can also be immobilized through grouting in the presence of high concentrations of nitrate, nitrite, and hydroxide ions. Pretreatment of the salt solutions with iron salts was investigated to determine whether additional benefit could be obtained through pretreatment of pertechnetate.

## EXPERIMENTAL

The composition of the simulant used in this study is provided in table I. This simulant had a density of  $1.22 \text{ g/cm}^3$ , a pH of 12.4, and  $\sim 1.8 \times 10^{-5} \text{ Ci/L}$  of Tc-99.

**Table I.** Composition of the salt waste stream that has been spiked with Tc-99.

Content	Components										
	H <sub>2</sub> O	NaNO <sub>2</sub>	NaNO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>	NaOH	NaAl(OH) <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>3</sub> PO <sub>4</sub>	NaCl	Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	Tc-99
wt%	71	3.0	14.0	2.5	2.5	3.0	2.5	0.5	0.5	0.38	$\sim 1.8 \times 10^{-4}$
M	-	0.54	2.04	0.22	0.78	0.32	0.29	0.04	0.11	0.05	$\sim 2.28 \times 10^{-5}$

Technetium-99 was measured by detecting its  $\beta$ -activity using a Quantulus-1220 spectrometer manufactured by Wallac of Finland (with an Optiphase HiSafe2 liquid scintillator). The error of the radiometric measurements was  $\pm 5\%$ , while the sensitivity of the measurements was 0.25 Bq per sample.

### **Tc-99 Pretreatment with Fe(+2) and Fe(+3)**

It has been shown that hydroxide precipitates, such as  $\text{Fe}(\text{OH})_x$ , are effective for co-precipitating Tc-99 as  $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$  under reducing conditions [2-6]. For example, introduction of  $\text{FeSO}_4$  into alkaline raffinates with a high Fe(III) content appear to be fairly effective in pertechnetate reduction/co-precipitation. However, as the  $\text{NaNO}_3$  concentration in the solution increases, the Tc sorption value decreases due to competition from nitrate ions [3, 5].

For the pretreatment experiments, 8 mL of the Tc-99 spiked simulant were placed into 12 mL plastic vials. Then, 0.2 mL of solutions of Fe(III) nitrate or Fe(II) sulfate were added as shown in table II. The vials were capped, shaken for 5 minutes, and centrifuged. The supernate was then sampled and the Tc-99 concentration,  $E_h$ , and pH were measured. Table II shows the results, along with the Tc-99 distribution coefficients ( $K_d$ ,  $\text{cm}^3/\text{g}$ ) calculated as a ratio of the Tc-99 concentration in 1g  $\text{Fe}(\text{OH})_x$  and its residual concentration in 1 mL of the solution.

**Table II.** Tc-99 Co-Precipitation from the doped simulant onto  $\text{Fe}(\text{OH})_x$ .

Sample	Carrier, g/L		Precipitating agent, g/L		After sorption		Tc-99 Concentration in BWS		$K_d$ , $\text{cm}^3/\text{g}$
					$E_h$ , B	pH	Prior to sorption, Bq/ml	After sorption, Bq/ml	
1	$\text{Fe}^{+3}$	1.00	-	-	0.064	12.31	637.4	560.3	69
2	$\text{Fe}^{3+}$	1.07	$\text{Fe}^{2+}$	1.05	0.042	12.60	589.3	96.4	1279
3	$\text{Fe}^{3+}$	1.21	$\text{Fe}^{2+}$	2.10	0.061	12.37	707.7	91.2	1070
4	-	-	$\text{Fe}^{2+}$	1.05	0.040	12.45	589.3	90.2	2771
5	-	-	$\text{Fe}^{2+}$	2.10	0.033	12.50	707.7	50.5	2170

The stability of the  $[\text{Fe}(\text{OH})_x \text{Tc}(\text{IV})]$  system to re-oxidation under aerobic conditions was determined by the following experimental process. Thirty mL of the spiked simulant were introduced into 50 mL vials and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was then added to achieve a final  $[\text{Fe}^{2+}]$  of 3.15 mg/mL. After 5 minutes of mixing, the vial was centrifuged to isolate the precipitate. Under these conditions, 99.4% of the Tc-99 was isolated with the precipitate. After decanting the solutions, the  $[\text{Fe}(\text{OH})_x(\text{Tc-IV})]$  precipitates remained in open vials for 15 hours. Next, 30 mL of distilled water were introduced into one of the vials, and 30 mL of the Tc-99 free simulant were introduced into the other vial. The vials were continuously shaken, and aliquots were taken after 1, 5, and 11 days, centrifuged, filtered and analyzed to determine the amount of Tc-99 re-oxidation to the soluble pertechnetate (see table III).

**Table III.** Tc-99 oxidation and desorption under aerobic conditions.

Leaching	% of sorbed Tc-99 released to solution		
	Day 1	Day 5	Day 11
Distilled water	0.25	-	2.1
Simulant	1.85	16.1	32.2

**Preparation of grout samples containing Tc-99**

Russian sources of cementitious materials were used for these experiments. They include blast furnace slag (BFS), M-500 Portland cement (PC), and metallurgical powder (MP). The reduction capabilities (R) of both BFS and MP were measured [7], using  $\text{KMnO}_4$  as an oxidizing agent, instead of  $\text{Ce(IV)}$ . The R value corresponds to the number of milliequivalents (meq) of  $\text{KMnO}_4$  that were used to oxidize 1 g of the BFS or MP. Table IV provides information on the cementitious materials.

**Table IV.** Major Compositions and Properties of Premix Components

Component	Content, wt %								Properties		
	$\text{SiO}_2$	$\text{CaO}$	$\text{MgO}$	$\text{Al}_2\text{O}_3$	$\text{Fe}_x\text{O}_y$	$\text{TiO}_2$	S	$\text{R}_2\text{O}$	R, meq $\text{g}^{-1}$	$S_s$ , $\text{cm}^2/\text{g}$	$\frac{\Sigma C + M}{\Sigma S + A}$
BFS	36.6	39.3	12.7	8.8	1.0	1.6	-	-	4.79	2800	1.46
PC	22.1	64.6	1.6	4.0	3.5	-	1.0	1.2	-	3960	2.9
MP	4.0	5.0	2.0	1.0	79.0	0.1	0.45	-	1.05	-	-

According to the XRD data, the slag is amorphous material with only 0.5 wt% of crystalline magnetic material consisting of  $\text{Fe}_3\text{O}_4$  (50%),  $\text{FeS}$  (30%), and  $\text{Fe}$  (20%). Sulfide inclusions were confirmed by detection of  $\text{H}_2\text{S}$  when diluted  $\text{HNO}_3$  was added to the BFS.

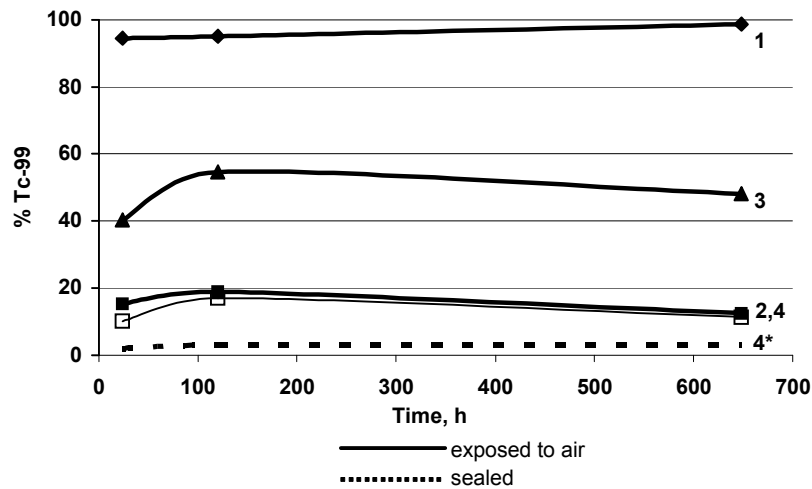
To prepare samples, the premix components were mixed with appropriate amounts of the simulant or the slurry produced by first adding  $\text{FeSO}_4$ . After 5 minutes of mixing, the fresh grout was poured into 4 cm tall, 2 cm diameter cylindrical molds. The water/premix mass ratio was between 0.4-0.5. Samples 1-4 were loosely covered with lids, while samples 4\* and 5 were sealed and not exposed to air. Table V presents data on the compositions of Samples 1-5.

**Table V.** Compositions of grout samples

Components		Sample Number				
		1	2	3	4; 4*	5
Liquid phase	Simulant with Tc-99	X	X	-	-	X
	Simulant with Tc-99 treated with FeSO <sub>4</sub> ([Fe <sup>+2</sup> ]=2 g/L)	-	-	X	X	-
Solid phase	PC	X	-	X	-	-
	PC:BFS = (25:75), wt.%	-	X	-	X	-
	PC:BFS:MP= (25:70:5), wt.%	-	-	-	-	X

**Crushed and monolithic leaching of cured grout samples containing Tc-99**

After 28 days of curing, samples 1-4 were leached using a modified ASTM D-5233 protocol [8] in which the grout was crushed to less than 2 mm with a mass of water to mass of solids ratio of 10. Figure 1 shows the Tc-99 leaching results over 27 days.



**Figure 1.** Tc-99 leaching from crushed grout samples as a function of time. (Numbers next to the curves correspond to the sample numbers in Table V.)

The ANSI/ANS-16.1 protocol [9] was used for the monolith leaching test (sample 5). The average Tc-99 effective diffusion coefficient, D, and leaching index, L, determined by this method are Deff of 4.8 x 10<sup>-12</sup> cm<sup>2</sup>/sec and L equal to 11.4.



## DISCUSSION

### Tc-99 leaching results

The accelerated Tc-99 leaching results using crushed samples reveal that blast furnace slag is the most effective component in the grout formulation for immobilizing Tc-99. Portland cement was not effective in reducing and immobilizing pertechnetate. In fact, as long as oxygen is excluded, the system containing BFS is stable over the time period of this test. (A 2% release of pertechnetate was observed for sample 4\* and this most likely is due to residual oxygen in the system.) On the other hand, an increased surface area (caused by the crushing of the grout) can lead to the re-oxidation of Tc (IV) to produce soluble pertechnetate in the presence of oxygen. Pretreatment of the waste with FeSO<sub>4</sub> did not improve the leaching performance of the grout waste form if blast furnace slag was present.

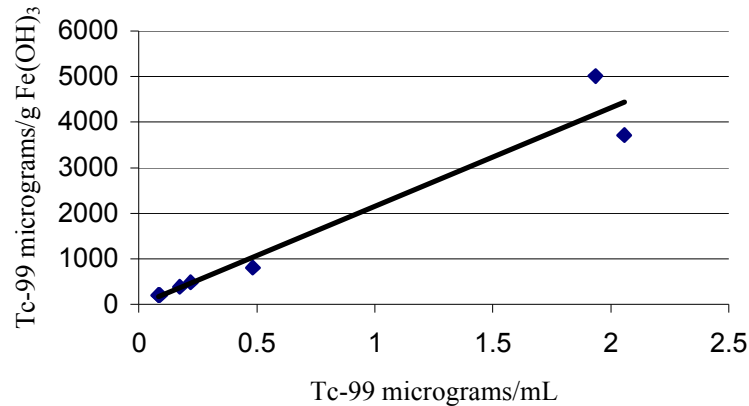
An effective diffusion coefficient of  $4.75 \times 10^{-12}$  (Leach Index of 11.4) was measured using the ANSI/ANS-16.1 protocol. These values are consistent with previous results for Tc-99 using a dilute salt solution as the waste stream [1]. The use of a simulant with a higher sodium Molarity of ~4 (typical of the salt waste stream that will be immobilized at the Saltstone Production Facility) demonstrates effective immobilization of Tc-99 in these slag containing formulations at higher salt concentrations.

### PORFLOW modeling

The diffusivity determined by the monolith leaching test was used as an input value into the flow and transport modeling for Tc-99 re-oxidation, diffusion and release from the grout waste form (e.g., a vault cell of dimensions ~ 30 x 30 x 6 meters). Sensitivity studies have been performed using a fixed value of diffusivity (as measured in this study) as a function of hydraulic conductivity and total reductive capacity of the waste form. For example, using the PORFLOW model, 35 % of the technetium would exit the waste form after 10,000 years if the hydraulic conductivity increased to  $1 \times 10^{-9}$  cm/sec. The results of this sensitivity study will be published separately.

### Tc-99 pretreatment

The highest  $K_d$  values for Tc were obtained using ferrous sulfate (see table II). This leads to a precipitate that contains the reduced pertechnetate. Figure 2 shows the dependence of Tc-99 equilibrium concentrations in the solid precipitate and in solution. This linear dependence corresponds to a  $K_d = 2200 \text{ cm}^3/\text{g}$  indicating that practically all of the Tc(IV) is present in the precipitate.



**Figure 2.** Equilibrium isotherm for Tc co-precipitation with  $\text{Fe(OH)}_x$  at room temperature.

However, in the presence of oxygen, re-oxidation and dissolution Tc(IV) occurs, with a color change from green that is characteristic of  $\text{Fe(OH)}_2$ , to black and then to reddish brown that is characteristic of  $\text{Fe(OH)}_3$ .

## CONCLUSIONS

A salt solution (doped with Tc-99), that simulates the salt waste stream to be processed at the Saltstone Production Facility, was immobilized in grout waste forms with and without (1) ground granulated blast furnace slag and (2) pretreatment with iron salts. The degree of immobilization of Tc-99 was measured through monolithic and crushed grout leaching tests. Although Fe (+2) was shown to be effective in reducing Tc-99 to the +4 state, the strong reducing nature of the blast furnace slag present in the grout formulation dominated the reduction of Tc-99 in the cured grouts. An effective diffusion coefficient of  $4.75 \times 10^{-12}$  (Leach Index of 11.4) was measured using the ANSI/ANS-16.1 protocol. The leaching results show that, even in the presence of a concentrated salt solution, blast furnace slag can effectively reduce pertechnetate to the immobile +4 oxidation state. The measured diffusivity was introduced into a flow and transport model (PORFLOW) to calculate the release of Tc-99 from a Saltstone Vault as a function of hydraulic conductivity of the matrix.

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