

Parametric Studies on the Use of In Situ Formed Magnetite for the Removal of Sr and Actinides from Tank Waste at the Savannah River Site¹

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PARAMETRIC STUDIES ON THE USE OF IN SITU FORMED MAGNETITE FOR THE REMOVAL OF Sr AND ACTINIDES FROM TANK WASTE AT THE SAVANNAH RIVER SITE

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ABSTRACT

This report discusses the experimental program conducted at ANL to study the performance of in-situ-formed magnetite for the removal of Sr, Pu, Np, U, Am, and Cs from the Savannah River Site (SRS) tank waste. The boundaries for the experimental work were defined based on the operational envelope developed earlier in collaboration with SRS. In situ formed "magnetite" is actually a mixture of Fe(II) and Fe(III) oxides and hydroxides, including magnetite. Decontamination factor (DF) values were measured for both magnetite and monosodium titanate (MST). Magnetite DF values were found to be superior to MST for all isotopes studied. DF values for Pu, Np, and Sr, achieved within 30 minutes of magnetite formation were orders of magnitude larger than the needed values. DF values for U and Am were less than the former three but still acceptable, and greater than MST. DF values for Cs were very low. Conditions were found under which magnetite filtered rapidly and faster than MST. Further tests are needed to make concrete conclusions on the magnetite performance relative to MST in a cross-flow filtration setup.

I. INTRODUCTION

Nearly 34 million gallons of radioactive waste are currently stored in tanks at the Savannah River Site (SRS) in South Carolina. This waste, which is a product of the cold-war era, contains a significant inventory of hazardous radioactive isotopes. Radionuclides of special concern are cesium (Cs), strontium (Sr), neptunium (Np), plutonium (Pu), and americium (Am). At the Savannah River Site (and similarly at the Hanford site), the plan is to

separate the waste into a high-level waste (HLW) stream, which will contain most of the Cs, Sr, and actinide elements, and a low-level waste (LLW) stream that contains a high fraction of the non-radioactive waste constituents. Because of the high cost associated with disposal of the HLW, it is essential to minimize its volume. The current SRS plan is to remove Sr and actinides (Pu, Am, Np) from the alkaline supernatant and salt cake dissolved using powdered monosodium titanate (MST) in a stirred tank [HOBBS-1992, -1993, and -1999]. Although uranium (U) is not an isotope of special concern, its removal by MST is tracked since it is present, on a mass basis, more than the other alpha emitters. However, according to SRS, uranium removal is not needed to meet the current regulatory commitments [FINK-2002].

A number of cost and technical risk issues are associated with the MST technology. The Salt Disposition System Engineering Team identified the adsorption kinetics for Sr and alpha emitters onto MST as a technical risk [RUTLAND-1998]. A number of studies have also shown that the uptake of actinides, especially Pu and Np, on MST is not adequate [BARNES-2002, ELDER-2001]. Additionally, the alpha emitters sorption process configuration in the current flowsheet for Caustic Side Solvent Extraction (CSSX) lacks flexibility and requires utilization of extremely large process equipment including the alpha sorption vessel, the cross-flow filters and the filter feed pumps [SUBOSITS-2000]. Finally, limited titanium solubility in the glass is another major process risk, which significantly limits the amount of MST that could be used. In order to reduce or eliminate the risks for the baseline Sr and actinide removal process, SRS is considering alternative technologies to replace the current MST technology [HOBBS-2000(a)]. These alternative technologies include using sodium nonatitanate (ST), SrTreat[®], crystalline silicotitanate, pharmacosiderites[®], and sodium permanganate. Some of these alternative materials performed better than MST in some aspects. However, in many cases, the overall performance has not significantly improved. For example, ST exhibited lower removal capacities than MST [HOBBS-2000(b)], while sodium permanganate removed Sr reasonably, but was much less encouraging for Pu and Np removal [BARNES-2002].

In situ formed magnetite was proposed by Argonne National Laboratory (ANL) as an alternative to MST for the removal of Sr and actinides. Magnetite is formed immediately in situ by adding solutions containing Fe(II) and Fe(III) ions to the alkaline medium. The magnetite particles then remove the Sr and actinides out of the solution during the precipitation process. In the first phase of this project, an operational envelope was developed in consultation with SRS to define the boundaries of the experimental work reported here [ARAFAT-2002]. The operational envelope defined the simulant to be used, radionuclides concentrations and oxidation states, decontamination factor (DF) requirements (Shown in Table 1), and the maximum amount of magnetite to be used. This report summarizes the findings of the first laboratory study using magnetite.

Table 1. Decontamination Factor Requirements for Various Radionuclides

Radionuclide	SRS DF Requirements (average/upper bound)	Minimum ANL DF Requirements for Magnetite Process
Sr	1/5.1	6
Pu/Am	12/49	50
Np	1/2	3
U	1/1	3

II. EXPERIMENTAL

A. Materials and Solutions

Alkaline waste simulant, identical to that used by SRS in the MST tests, was used. The recipe for simulant preparation was provided by SRS [ARAFAT-2002] (shown in Appendix A). In order to provide greater accuracy and ease of analysis by using gamma spectroscopy and liquid scintillation counting techniques, to measure the concentrations of individual radionuclides, we modified the SRS recipe. The five radionuclides (U, Sr, Pu, Am, Np) were not added to the simulant at once, as discussed next.

Initially, a 1.2-L batch of nitric acid and aluminum nitrate was prepared. The nitric acid solution was split evenly into two batches, each batch sufficient to prepare one liter of simulant. One of these batches was used to prepare a “cold” simulant (i.e. with no radionuclides present). To the other batch, 9.9 mg of depleted uranium (DU), as uranyl nitrate hexahydrate (UNH), were added. This bottle was then split into four equal batches (~150 mL each) so that each would be enough to prepare a 250 mL batch of alkaline simulant. The DU was present in all simulants to minimize differences in actinide mass among the simulants. The first simulant contained U-233 to facilitate liquid scintillation counting of uranium. Samples of the alkaline filtered solution were counted against earlier acidic samples to verify that DU did not contribute significantly to the counting results. The amount of U-233 added to the solution was 0.18 mg, measured by liquid scintillation. The U-233 stock solution was also counted using alpha spectrometry and its purity from daughter nuclides was verified. With the U-233 addition, the total UNH concentration in this simulant rose to 11.5 mg/L. The second simulant contained plutonium at 0.2 mg/L. The plutonium stock was purified by ion exchange to remove Am-241 and other impurities/decay products. Liquid scintillation was used to analyze these samples. The third simulant contained 0.2 mg/L Am-241, 0.5 mg/L Np-237, and tracer quantities of Np-239 and Sr-85. Strontium was present at 0.6 mg/L, using a stable strontium nitrate. Due to the short half-lives of Np-239 and Sr-85, the mass added in the radiotracers is negligible. Gamma spectroscopy was used to analyze these samples, with the peaks of interest appearing at 59.6, 103.8, and 514.0 keV, for Am-241, Np-239, and Sr-85, respectively. The fourth simulant batch was kept as a spare and was never used. After adding the radionuclides, the simulant preparation was completed according to the recipe in Appendix A. The sodium carbonate solution used in the simulant was pre-treated with monosodium titanate received from SRS to remove any strontium impurities that may be

present in the stock chemical [HOBBS-2002]. The isotopes used in this study were purified using the methods detailed in Appendix B.

Monosodium Titanate (MST) was obtained from SRS in a slurry form. The MST solid content of the slurry was measured upon its receipt and found to be 18.2%. Magnetite was formed in situ in the alkaline simulant by adding a mixture of Fe(II) and Fe(III) solutions to provide the desired iron concentration in the simulant. This Fe(II)/(III) mixture solution was prepared by mixing known amounts of 1 M $\text{Fe}(\text{NO}_3)_3$ (in DI water) and 1 M FeSO_4 (in 0.5 M sulfuric acid). It was noticed that when the Fe(II) solution is stored for long periods, some of the Fe(II) strongly oxidizes to Fe(III). For example, when the FeSO_4 solution (before mixing with $\text{Fe}(\text{NO}_3)_3$) was stored for five weeks and then titrated again, it was found that 3% of the Fe(II) was oxidized to Fe(III). Finally, some limited tests were performed using commercial magnetite, purchased from Fischer Scientific Co.

B. Magnetite Characterization

Precipitation tests were performed to determine the optimal conditions for magnetite formation. Tests were performed in centrifuge tubes, usually with 5 mL initial simulant solution. After precipitation, the precipitate was centrifuged and washed with 5 mL portions of water twice, then with 5 mL portions of 1% NH_4Cl solution until the pH of the wash reached 7. After two water washes, the precipitate would usually peptize but the NH_4Cl solution prevented this. The magnetic property of the precipitate was checked qualitatively by the response of the settled precipitate to a small horseshoe magnet. During these tests, the color of the precipitate was observed as well as the occasional formation of a thin reddish-colored layer characteristic of ferric hydroxide.

X-Ray Diffraction (XRD) characterization of the precipitate was performed using a Rigaku Diffractometer with Cu radiation. The data were collected from 10 degrees to 75 degrees in two theta. The step size was 0.03 degrees and the scan speed was 1.5 degrees / minute. Patterns were interpreted by comparison with International Center for Diffraction Data (ICDD) powder patterns.

Particle size distribution of the magnetite particles formed in situ in the simulant was measured. This was done by injecting an iron solution mixture, with the desired Fe(II):Fe(III) ratio, into a 10-mL simulant sample to give a total of 2.2 mg Fe/mL solution. The solution was then turned end-over-end several times to achieve adequate shaking. A sample of the resulting suspension was then injected into a Light-Scattering Particle Size Analyzer, a Beckman-Coulter counter (Model LS100Q, Fullerton CA). Its effective measuring range is from 1 to 1000 μm .

C. Decontamination Factor (DF) Measurements

DF tests for radioisotopes removal by both magnetite and MST were performed to allow the comparison of magnetite and MST performance under identical conditions. The tests were done as follows. A pre-determined amount of the carrier (MST, commercial magnetite, or Fe(II)/Fe(III) mixture solution) was added to a number of 8 mL centrifuge

tubes, each containing 5 mL of simulant with the isotope(s) to be studied. In the case of Fe(II)/(III)solution, magnetite precipitates formed immediately upon addition to the simulant. The tubes were then placed on a rotating shaker. At pre-determined time intervals, one tube was removed from the shaker (in few cases, two tubes were sampled simultaneously, presenting a duplicate data point). The solution was centrifuged for few minutes, filtered through a nylon 0.2 μm syringe filter, and a sample was taken from the supernatant. The concentration(s) of radionuclide(s) in the supernatant were then measured using either liquid scintillation or gamma spectroscopy, as detailed in Section A above. Decontamination factors were calculated by dividing the initial isotope concentration by its final concentration in solution after treatment.

All the DF tests involving magnetite were performed using 2.2 mg Fe/mL, as specified in the operational envelope [ARAFAT-2002]. The maximum iron concentration was chosen to provide the best case for a proof-of-concept for the magnetite process. DF tests using MST were less straightforward. Since MST was received in a slurry form, it was critical to find an appropriate method to weigh a precise quantity of MST to be used in the DF tests. High-temperature drying of slurry, to produce the MST powder, was unfavorable since it could change the properties of hydrated MST particles. As an alternative, MST slurry was filtered, using a 5- μm polycarbonate filter membrane, followed by particle washing with DI water and re-filtration. MST particles, accumulated on the filter membrane, were then collected, weighed, and added to the simulant to produce a 0.4 g MST/ L simulant. A pre-weighed sample of the filtered MST was placed in a desiccator to determine its moisture content. After drying for 24 hours in the desiccator, the dry MST particles were weighed. It was found that the sample mass dropped by 50%. Therefore, our tests were seen as using an MST-solid concentration of 0.2 mg of dehydrated MST/mL simulant.

D. Filtration Studies

Filtration studies were performed both under gravity and 29 inch of vacuum. In gravity filtration tests, we used a cellulose filter paper, Whatman No. 40, which is a quantitative (ashless) paper of medium porosity (average pore size = 8 μm). The paper, 11 cm in diameter, was folded, placed in a polyethylene funnel (8 cm top diameter), and wetted with water. The water was allowed to drain completely before use. The funnel had a short wide stem, so a column of filtrate could not form in the stem and affect the filtration rate. Approximately 10 mL of the solution was added to the funnel and the filtrate collected in a 10 mL graduated cylinder. The filtration time was measured with an electronic stopwatch. The iron solutions were prepared by mixing appropriate volumes of 1M ferric nitrate in water and 1M ferrous sulfate in a 0.5 M sulfuric acid and adding the mixture rapidly to 10 mL of simulant and shaking the tube vigorously. The total iron concentration was 2.2 mg/mL.

The filtration studies under vacuum were performed using membrane filters. Filters with pore sizes of 0.45, 5, 20, and 41 μm were used. The filters were made from polycarbonate (PC), nylon, or polyvinylidene fluoride (PVDF). The filtration through membrane filters was conducted using 25-mm diameter filters with typical glass chimney equipment, the filter was clamped between a sintered glass disk and a chimney engraved with

1 milliliter markings. In limited cases, magnetite particles were flocculated by heating to 45°C overnight followed by filtering.

III. RESULTS AND DISCUSSION

A. Magnetite Formation

Seven tests were performed to investigate the effects of different operating parameters on magnetite formation in situ in the waste simulant. All these tests were performed using an Fe(II):Fe(III) ratio of 1:2. These tests are summarized in Table 2.

Table 2. Effect of Different Parameters on Magnetite Formation in SRS Simulant

Test No.	Iron ^a concentration (mg Fe/mL)	Precipitate color	Precipitate response to magnet	Fe(OH) ₃ Layer? (Y/N)	Notes
1	7.3	Black	Weak	N	--
2	3.7	Green to Black	Weak	Y	Fe solution added dropwise to simulant
3	7.3	Green to Black	Weak	Y	Simulant added to Fe solution
4	7.3	Green to Black	Negligible	Y	FeSO ₄ solution in water instead of H ₂ SO ₄ solution
5	7.3	Green to Black	Negligible	Y	FeSO ₄ solution in water instead of H ₂ SO ₄ solution, Iron solution added dropwise to simulant
6	7.3	Green to Black	Negligible	N	Precipitated at 50 °C then allowed to settle at 50 °C for 40 minutes
7	7.3	Green to Black	Negligible	Y	Fe(III) added as Fe ₂ (SO ₄) ₃ instead of Fe(NO ₃) ₃

^a Added as a 1:2 mix of FeSO₄ and Fe(NO₃)₃

As the iron solution (mixture of Fe(II) and Fe(III) ions) was added to the alkaline solution, the precipitate formed initially near the surface of the liquid and continued downward as the solutions were mixed. In some cases, a small amount of green precipitate was observed very close to the surface. This green precipitate is ferrous hydroxide, Fe(OH)₂. This is indicated in the third column of Table 1 as “Green to Black”. This green precipitate disappears upon mixing and all precipitates became very black. In some cases, a reddish precipitate layer was seen at the top of the centrifuged precipitate. This must be due to the formation of ferric hydroxide, Fe(OH)₃, which cannot be seen in the presence of a much larger amount of the intensely black precipitate until centrifugation separates the two on the basis of density. Except as noted, the iron solution was added rapidly. Also, Fe(III) was added as a ferric nitrate solution, in DI water, and Fe(II) was added as ferrous sulfate solution in 0.5 M sulfuric acid, unless noted otherwise.

By examining Table 2, a number observations can be made about magnetite formation in the simulant solution. First, although the precipitate is black, its response to a magnet is

either weak or negligible, contrary to magnetite characteristics. This indicates that the iron precipitate is not pure magnetite but was more likely a mixture of magnetite and other precipitates, such as hydrated ferric oxide and maghemite (Fe_2O_3), which also gives a black precipitate if a small amount of ferrous ion is incorporated, due to electron transfer between the Fe(II) and Fe(III). This conclusion is further supported by XRD data, which will be discussed later. However, for simplicity, the iron precipitate mixture will be referred to as “magnetite” throughout this report.

Second, a number of changes led to the formation of $\text{Fe}(\text{OH})_3$. These changes are adding the iron solution slowly (dropwise) to the simulant, adding Fe(II) in water instead of the 0.5 M H_2SO_4 solution, and adding Fe(III) as ferric sulfate instead of ferric nitrate. It is not fully understood yet why these changes affect magnetite formation. An eighth test was performed (not shown in Table 2) using an iron mixture solution with Fe(II):Fe(III) ratios other than 1:2. Three new ratios were used. These are 100:3, 10:1, 1:1, and 5:1. Based on the precipitate response to a magnet, the amount of magnetite formed in all these tests was qualitatively judged to be greater than that formed using the Fe(II):Fe(III)=1:2 ratio.

As an attempt to gain some insight on the mechanism of magnetite formation, some precipitation tests were performed using NaOH solution instead of the simulant. The outcome of these tests is summarized in Table 3. These results show that the precipitate’s magnetic response is stronger in all cases than that formed in the simulant, which indicates greater magnetite formation. This is also supported by the absence of any $\text{Fe}(\text{OH})_3$ formation, as observed from the sixth column in Table 3. It is speculated that the presence of oxidizing agents, like the nitrate ion, are likely to affect magnetite formation. Further studies would be needed to explore the mechanism of magnetite formation in the alkaline waste.

Three X-Ray Diffraction (XRD) tests were performed using commercial magnetite, magnetite formed in situ in waste simulant, and magnetite formed in situ in NaOH solution. The XRD patterns for these three samples are shown in Figures 1-3, respectively, along with XRD standard patterns for some iron compounds, for comparison purposes. Commercial magnetite XRD analysis was conducted for comparison purposes and was found to give a well-defined peak pattern, which is anticipated for a crystalline material (Fig. 1). The pattern for the simulant precipitate, on the other hand, is broader. This indicates a material which is less pure and more amorphous. It is interesting to notice that maghemite (Fe_2O_3) has an XRD pattern very close to magnetite (Fe_3O_4). The possibility of maghemite formation was discussed earlier in this section. The XRD pattern for iron precipitate in NaOH solution (Fig. 3) shows peaks that are more defined and less broad than those for the simulant (Fig. 2). This is in agreement with the precipitation tests discussed earlier, which showed that more magnetite forms in NaOH solution than in the simulant.

Table 3. Effect of Different Parameters on Magnetite Formation in NaOH Solution

Test No.	Iron concentration (mg Fe/mL)	NaOH concentration (M)	Precipitate color	Precipitate response to magnet	Fe(OH) ₃ Layer? (Y/N)	Notes
1	7.3	6	Black	Strong	N	--
2	7.3	1	Green to Black	Strong	N	--
3	7.3	2	Black	Strong	N	--
4	7.3	4	Black	Strong	N	--
5	7.3	6	Black	Weak to Strong	N	response to magnet increased over few hours
6	7.3	6	Green to Black	Strong	N	FeSO ₄ solution in water instead of H ₂ SO ₄ solution
7	7.3	6	Black	Strong	N	FeSO ₄ solution in water instead of H ₂ SO ₄ solution, Iron solution added dropwise
8	7.3	6	Green to Black	Strong	N	Precipitated at 50 °C then allowed to settle at 50 °C for 40 minutes

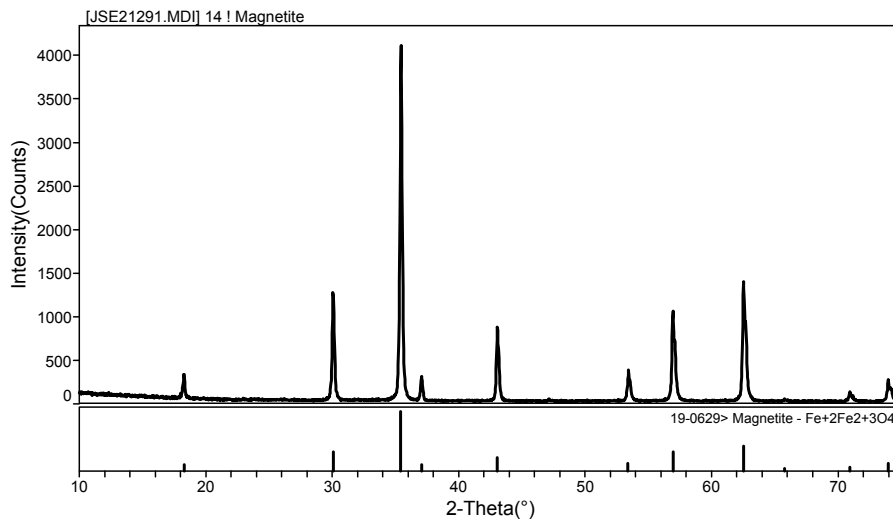


Figure 1. XRD Pattern for Commercial Magnetite

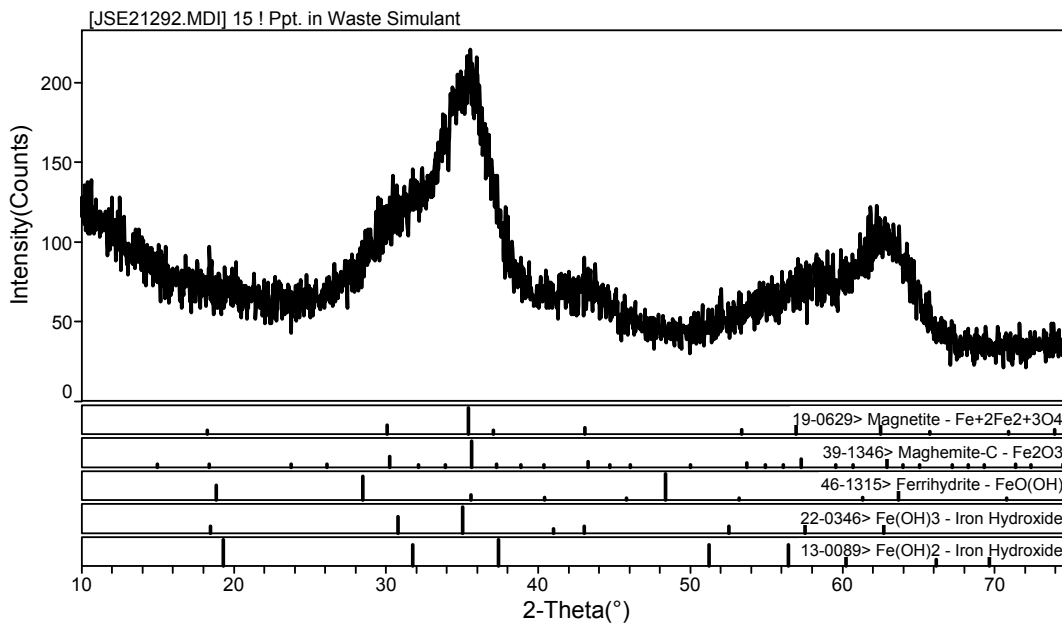


Figure 2. XRD Pattern for Magnetite Formed In Situ in Waste Simulant

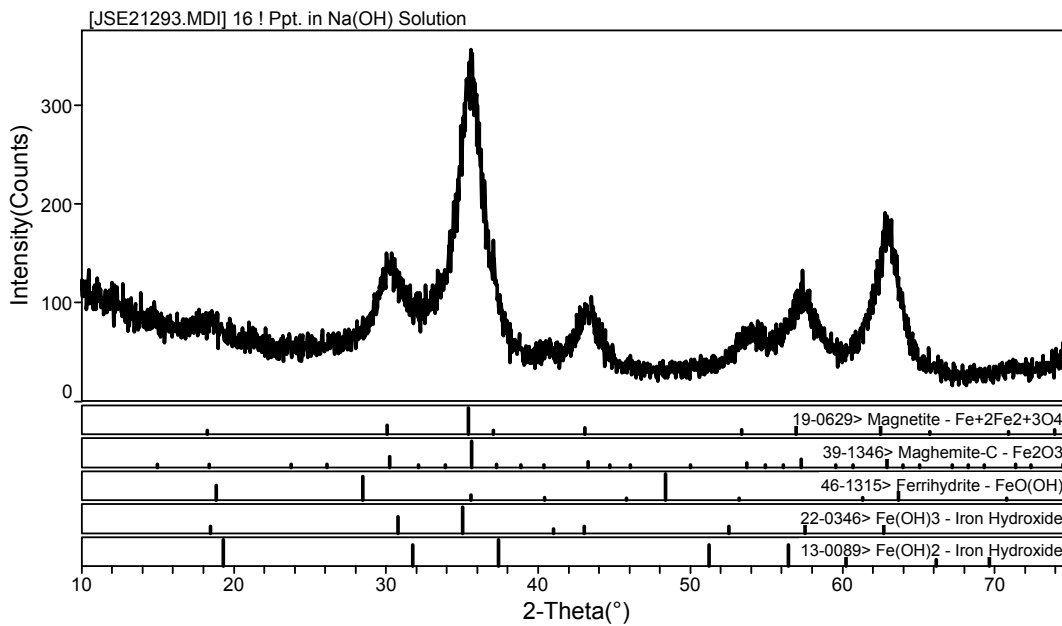


Figure 3. XRD Pattern for Magnetite Formed In Situ in NaOH Solution

Particle size distribution analysis was performed for magnetite precipitates in the waste simulant solution using three different Fe(II):Fe(III) ratios. Duplicate samples were done for every ratio and the distributions for the duplicates were basically identical. These ratios are 1:2, 1:1, and 1:0. The particle size distribution for all three ratios is shown in Fig. 4. The distribution was fitted automatically by the coulter counter machine using a built-in model. The mean particle size for the three distributions is 47, 49, and 61 μm , respectively. Some statistics on the size distributions are also provided in Table 4. Additionally, the magnetite precipitate has a significantly larger particle size than the MST (average size about 7 μm , as established by SRS). However, the size distribution of the precipitate particles is very likely to depend on other factors such as mixing time, mixing intensity, temperature, and the use of flocculants. These factors are recommended for further studies.

Table 4. Particle Size Distribution Statistics for Magnetite Particles in the Waste Simulant

Volume % of particles	Particle diameter (μm)		
	Fe(II):Fe(III) = 1:2	Fe(II):Fe(III) = 1:1	Fe(II):Fe(III) = 1:0
10	10	12	9
25	19	22	20
50	37	42	43
75	63	68	79
90	97	98	134

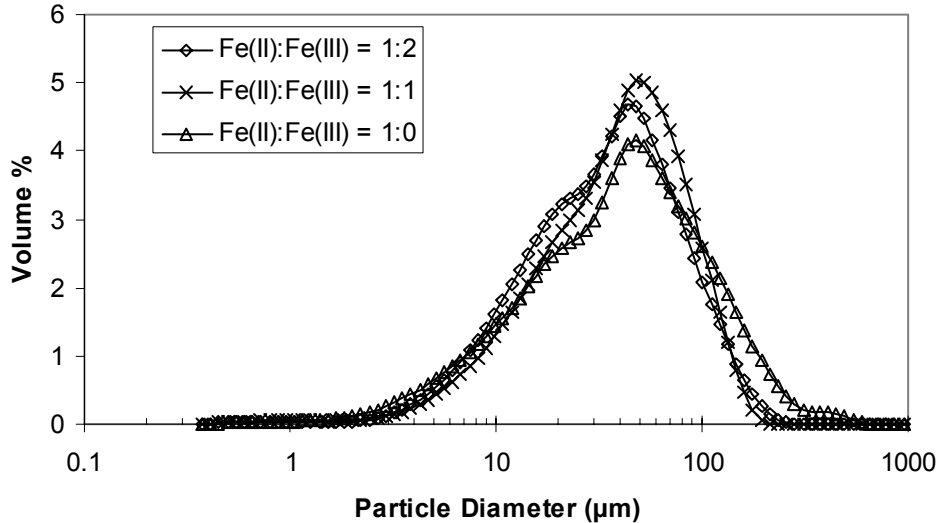


Figure 4. Particle Size Distribution of the Magnetite Particles in Waste Simulant

B. Sr and Actinides Removal Using Magnetite

Figure 5 shows the first set of decontamination factor (DF) tests for Pu(IV). This test went for a short time (1.5 hours) and was intended to find the Fe(II):Fe(III) ratio that will yield the best DF results. The total iron concentration in solution in these tests is 2.2 mg-

Fe/mL, which is the maximum acceptable amount [ARAFAT-2002] based on forming magnetite crystals only. For all DF tests discussed in this section, iron was added to the solution at this concentration. As evident from Fig. 5, the best DF results were achievable using Fe(II):Fe(III) ratio of 1:2 or 1:1, while lower DF values were obtained using Fe(II):Fe(III) = 1:0. Based on this preliminary test, it was decided that all following tests will be performed using the Fe(II)/(III) ratios of 1:1 and 1:2 only.

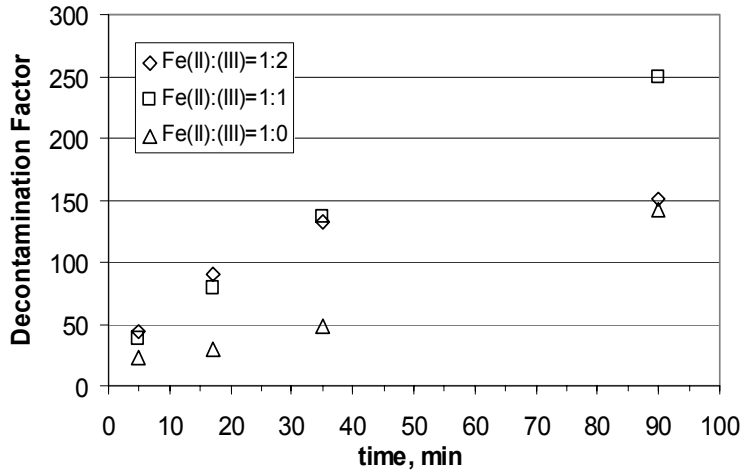


Figure 5. A Preliminary Test to Determine the Best Fe(II)/(III) Ratio Using Pu(IV) DF Values

A second test was performed using commercial magnetite for Pu removal. DF results for this test are shown in Fig. 6. Although DF values were still on the rise after 90 minutes of magnetite contact, these values were still very low (less than 1.2), which discouraged us from studying commercial magnetite any further and focusing instead on in situ formed magnetite. The poor performance of commercial magnetite (Fig. 6), compared to in situ formed magnetite (Fig. 5) gives some insight on the Pu removal mechanism. One possibility is that Pu ions are incorporated into the magnetite structure as it forms (i.e. co-precipitation mechanism). An alternative is that Pu is being removed by surface adsorption on the magnetite surface. If this is the case, the results in Fig. 6 strongly suggest that the formation method for magnetite has a strong effect on the available adsorption surface, where pre-formed magnetite has less adsorption capacity than the in situ formed magnetite. This is so because commercial (pre-formed) magnetite is a crystalline material with a small surface area. The third possibility is that other iron precipitates, which co-precipitate with magnetite, are the primary drive behind the removal. Within the scope of this work, it was not possible to further investigate the actual decontamination mechanism.

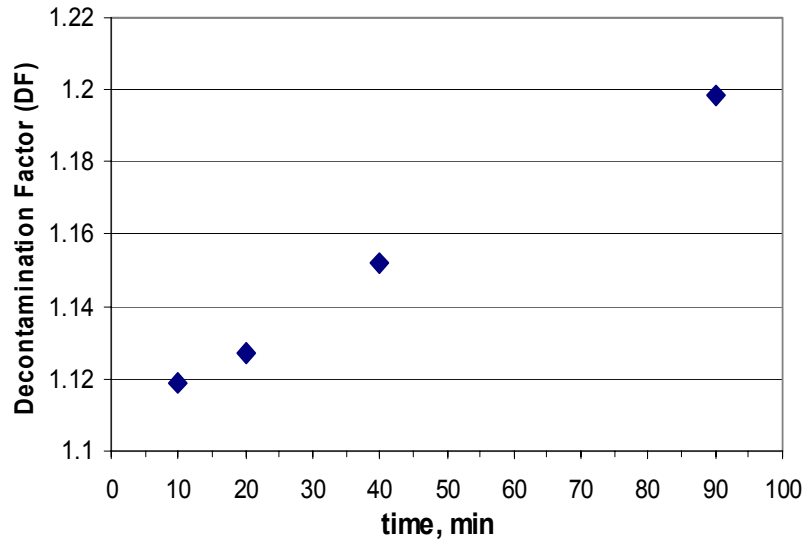


Figure 6. Pu (IV) Removal Using Commercial Magnetite

A second test using in situ formed magnetite for Pu removal was conducted and was extended to 48 hours. Results for this test are shown in Fig. 7. Figure 7 shows that magnetite, at either Fe(II)/(III) ratio, achieves DF values two orders of magnitude higher than those achieved by MST. More importantly, these high DF values are achieved within 30 minutes of magnetite formation, as summarized in Table 5. After 30 minutes, DF values go down until they reach a plateau, but are still very high compared to MST and are, by far, higher than the bounding DF value targeted by SRS (Table 1). Another interesting observation is that iron solution with Fe(II)/(III) = 1:1 yielded higher DF values than the solution with Fe(II)/(III) = 1:2. This was found to be the case for all radionuclides tested, as will be shown shortly.

Table 5. DF values for Pu(IV)

time (hr)	Decontamination Factor (DF)		
	MST	magnetite, Fe (II):Fe(III) = 1:2	magnetite, Fe (II):Fe(III) = 1:1
0.5	1.3	195	526
1	1.5	187	445
2	1.6	204	395
4	2.9	171	312
24	2.7	203	204
48	5.1	210	212

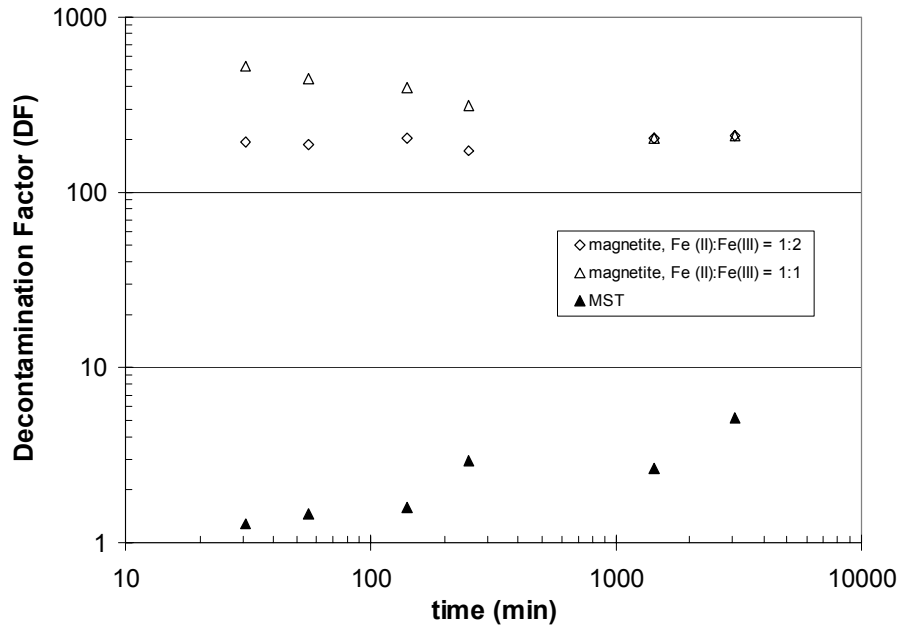


Figure 7. Pu(IV) Removal Using In Situ Formed Magnetite

DF values for Np(V) are shown in Fig. 8 and are also shown in Table 6. Similar to Pu(IV), DF values for magnetite are, by far, higher than those for MST and exceed the upper bound requirement set by SRS (Table 1). Trends similar to those for Pu are also observed for Np including decreasing DF values over time until a plateau is reached and higher DF values using Fe(II)/(III) ratio of 1:1.

Table 6. DF values for Np(V)

time (hr)	Decontamination Factor (DF)		
	MST	magnetite, Fe (II):Fe(III) = 1:2	magnetite, Fe (II):Fe(III) = 1:1
0.5	1.3	64	136
1	1.4	38	134
2	1.4	33	55
4	1.8	32	38
24	4.3	29	29
93	6.2	23	25

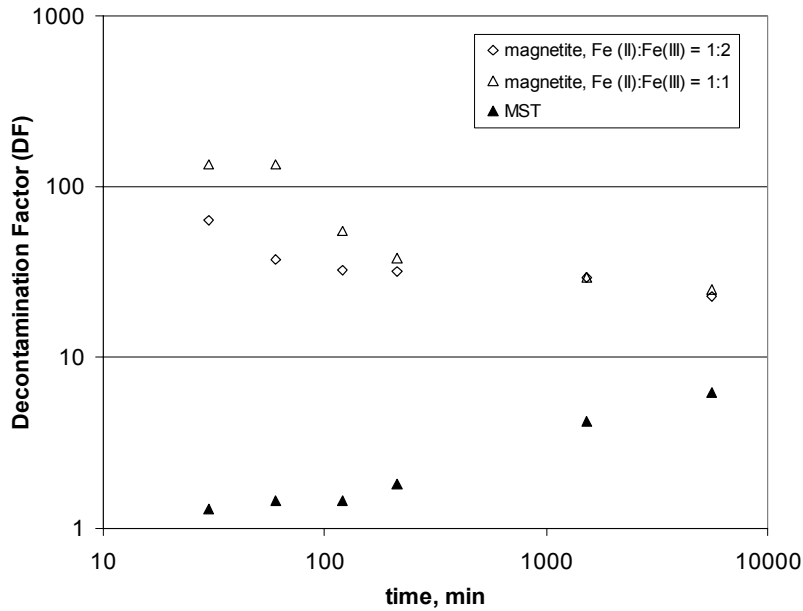


Figure 8. Np(V) Removal Using In Situ Formed Magnetite

The highest DF values using magnetite were achieved for Sr. Fig. 9 shows the change in DF values for Sr over a 93-hour period using both magnetite and MST. These values are also shown in Table 7. DF values using magnetite were three orders of magnitude larger than those achieved using MST. DF values of about 1000 were obtained within 1 hour of magnetite formation. The DF values then continued to rise over time and reached about 1800 within 4 hours and about 2200 within 24 hours. The current upper bound DF requirement for Sr is about 6.

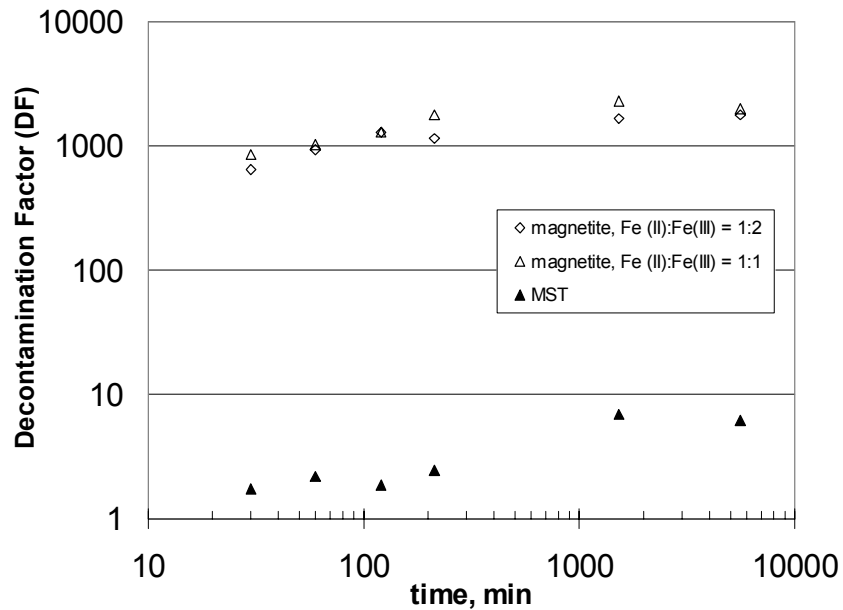


Figure 9. Sr Removal Using In Situ Formed Magnetite

Table 7. DF values for Sr

time (hr)	Decontamination Factor (DF)		
	MST	magnetite, Fe (II):Fe(III) = 1:2	magnetite, Fe (II):Fe(III) = 1:1
0.5	1.8	646	851
1	2.2	923	1022
2	1.9	1277	1288
4	2.4	1148	1786
24	6.9	1676	2269
93	6.2	1786	2017

DF tests for Am(III) and U(VI) are shown in Figures 10 and 11 and are also shown in Tables 8 and 9, respectively. For both isotopes, the DF values achieved using magnetite were higher than those achieved using MST. However, these DF values were not as high as the ones for Pu, Np, or Sr. DF values for Am ranged from about 2.5 in 30 minutes up to 7 in 24 hours and then up to 13 within 93 hours. The DF trend for Am(III) shows no plateau. However, it will not be practical from a process standpoint to process the waste for longer than 93 hours to achieve higher DF values. Uranium exhibited the lowest DF value of 1.5 at 30 minutes. The DF then decreased to 1.3 in 4 hours and then to 1.2 in 48 hours, and became comparable to MST. Although these values are low, its effect on the final process selection is expected to be marginal since, according to SRS, uranium removal is not needed to meet the current regulatory commitments [FINK-2002].

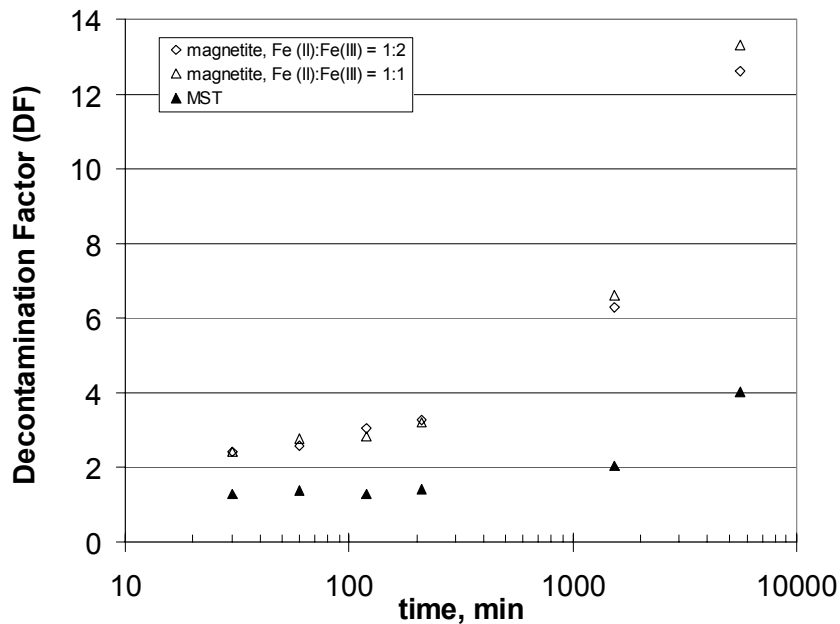


Figure 10. Am(III) Removal Using In Situ Formed Magnetite

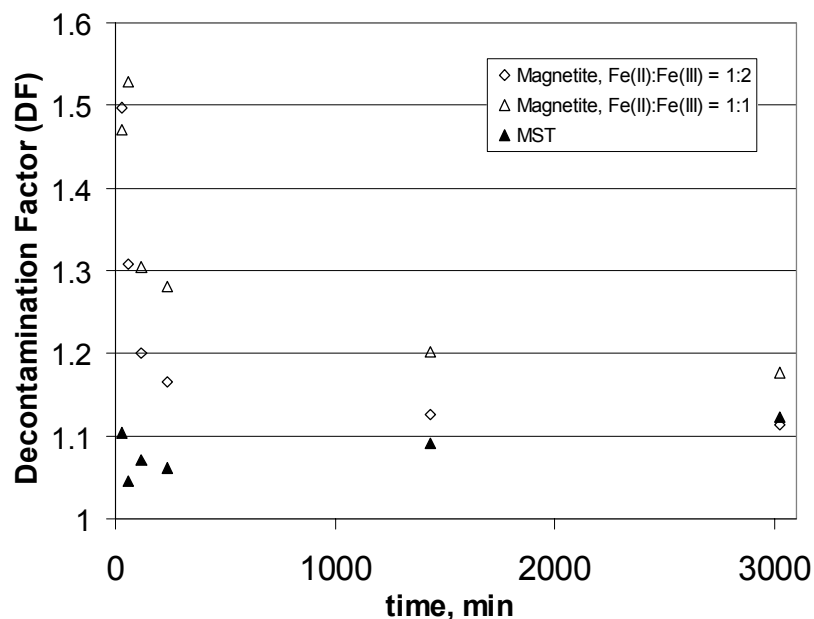


Figure 11. U(VI) Removal Using In Situ Formed Magnetite

Table 8. DF values for Am(III)

time (hr)	Decontamination Factor (DF)		
	MST	magnetite, Fe (II):Fe(III) = 1:2	magnetite, Fe (II):Fe(III) = 1:1
0.5	1.3	2.4	2.4
1	1.4	2.6	2.8
2	1.3	3.1	2.8
4	1.4	3.3	3.2
24	2.1	6.3	6.6
93	4.0	12.6	13.3

Table 9. DF values for U(VI)

time (hr)	Decontamination Factor (DF)		
	MST	magnetite, Fe (II):Fe(III) = 1:2	magnetite, Fe (II):Fe(III) = 1:1
0.5	1.1	1.5	1.5
1	1.0	1.3	1.5
2	1.1	1.2	1.3
4	1.1	1.2	1.3
24	1.1	1.1	1.2
48	1.1	1.1	1.2

Some insight on the causes behind the DF trends observed in this study can be gained by considering what is known about the chemistry of actinide removal using iron compounds. Low decontamination factors for U(VI) are consistent with the literature data on the co-precipitation of penta- and hexavalent actinides with Fe(III), Cr(III), Co(II) and (III) hydroxides from alkaline solutions [KROT-1996]. Using the Mössbauer effect method, it was shown that penta- and hexavalent Np hydroxides, containing NpO_2^{+2+} group, do not form mixed hydroxide phase with Fe(III) hydroxide in the course of their co-precipitation in alkaline media, but probably adsorb on the iron hydroxide's surface [GRIGORIEV-2001]. In contrast, tetravalent Pu and Np do form mixed hydroxides with Fe(III), resulting in highly efficient decontamination of the basic solutions. This explains why the DF values obtained for Pu(IV) were so high while those for U(VI) were low. The question then is: why did pentavalent Np(V) have such high DF values, which are considerably higher than those for U(VI), but yet lower than Pu(IV). This experimental observation can be explained by the reduction of Np(V) to Np(IV) by Fe(II), which was added together with Fe(III) to the simulant to form the magnetite. According to the thermodynamic data, such redox reduction is feasible ($\Delta E = +0.41$ V): the standard potential of the Fe(III)/Fe(II) couple in base is -0.56 V, the potential of the Np(V)/(IV) couple in base was estimated to be about -0.15 V [GELIS-2001]. However, the waste simulant solution contains some oxidizing agents like nitrate ions and dissolved oxygen, so, the reduction of Np(V) to Np(IV) probably was not complete, resulting in lower DF values for Np than for Pu(IV), but higher than U(VI).

Finally, a test was done to determine if magnetite shows any effectiveness in removing cesium (Cs-137) from the waste solution. The simulant (with DU and U-233) was spiked with Cs-137 at 0.7 mg/L (trace level). Magnetite was then formed in situ at 2.2 mg Fe/mL simulant. Two samples were then taken for analysis, one at 20 minutes and the second at 23 hours. DF values for these two samples were found to be 1.125 (± 0.08) and 1.147 (± 0.09), respectively. The adsorption of Cs hydroxide from alkaline solutions is known to be rather poor due to the high concentration of NaOH. Generally, to remove Cs from the waste, a formation of an insoluble Cs compound, or a different techniques such as solvent extraction, is needed.

C. Magnetite Filtration Studies

One of the technical limitations of the MST process is the filtration of the MST particles out of the treated waste solution. Cross-flow filtration is the process currently considered. As part of this work, we performed filtration tests to compare of the performance of magnetite to that of MST. Two types of filtration tests were done; gravity filtration using filter paper and vacuum filtration using membrane filters. However, neither test can be directly used to make any design decision related to the cross-flow filter. A well planned series of tests is needed before any judgment can be made about the magnetite filtration performance. Gravity filtration tests were done using a Whatman-40 filter paper, with an average pore size of 8 μm . Fig. 12 shows five gravity filtration tests. The volume filtered is plotted vs. time. Four of the tests were done using magnetite or MST particles at a concentration of 2.2 g Fe or MST/L. The fifth test was done using blank simulant with no precipitate.

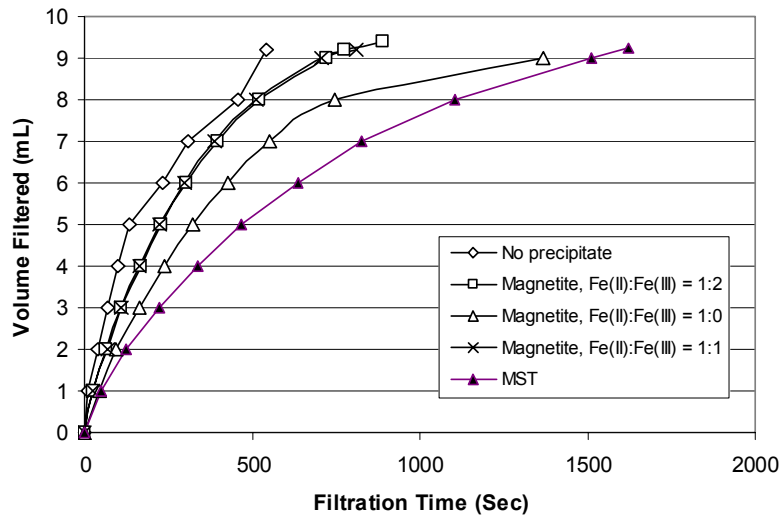


Figure 12. Filtration Studies Using Whatman-40 Filter Paper at 2.2 g Fe or MST/L

As expected, the fastest filtration rate was for the blank simulant where no particle resistance is present. MST exhibited the lowest filtration rate. The rates for the magnetite-containing solutions were between the two extremes. The best rates for magnetite were achieved using the Fe(II)/Fe(III) ratios of 1:2 and 1:1. The filtration rates for these two solutions were slightly lower than the blank solution, indicating that little resistance is caused by the presence of the magnetite particles. The third magnetite solution, with Fe(II)/Fe(III) = 1:0, also filtered faster than MST but was slower than the other two magnetite solutions.

The first filter membrane test was done using a 5.0- μm pore size polycarbonate membrane under 29 inch Hg vacuum. Although polycarbonate membrane filters were used in this study for comparison purposes, it should be mentioned that polycarbonate can be affected by the alkalinity of the waste after a period of contact with the solution and cannot, therefore, be used in real application. Two solutions were tested, one containing 2.2 g MST/L and the other containing magnetite, formed using Fe(II):Fe(III) ratio of 1:2 at a concentration of 2.2 g Fe/L. Fig. 13 shows the filtration rates for these two tests. It is observed from Fig. 13 that the filtration rates for MST and magnetite are not as different as the rates when filter paper was used. Initially, higher filtration rates are observed for magnetite. Then the two rates become closer to each other till they become similar. The opposite trend was observed using a 0.45 μm nylon membrane, where the MST-containing solution exhibited the fastest filtration rate, followed by a magnetite solution formed using Fe(II):Fe(III) = 1:2. The slowest rate was then observed for the solution containing magnetite formed using Fe(II):Fe(III) of 1:1 (Fig. 14). The difference in relative filtration rates between the three filters, the Whatman-40, the 5- μm , and 0.45- μm membranes, is attributed to the particle sizes. While MST has an average particle size of 5-7 μm , the average size for magnetite is about 45-60 μm , as discussed in Section III-B. The larger magnetite particles should facilitate the filtration, as observed, when a relatively large pore size filter was used (the Whatman-40 paper). However, when a very small pore size was used, as is the case of the 0.45- μm membrane, the larger magnetite particles blocked the filter pores and caused the drop in filtration rate. As expected, the filter material also has an effect. When a 0.45- μm polyvinylidene fluoride (PVDF) filter membrane

was used, as shown in Fig. 15, the filtration rate for magnetite formed using either Fe(II):Fe(III) = 1:2 or 1:1, were almost identical, whereas these rates were significantly different when a nylon filter of the same size was used (Fig. 14).

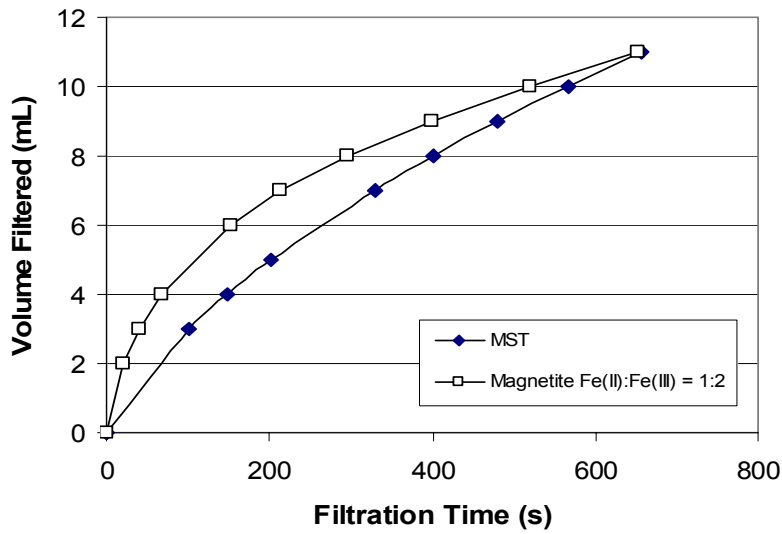


Figure 13. Filtration Studies Using 5.0-µm Polycarbonate Membrane Filter at 2.2 g Fe or MST/L

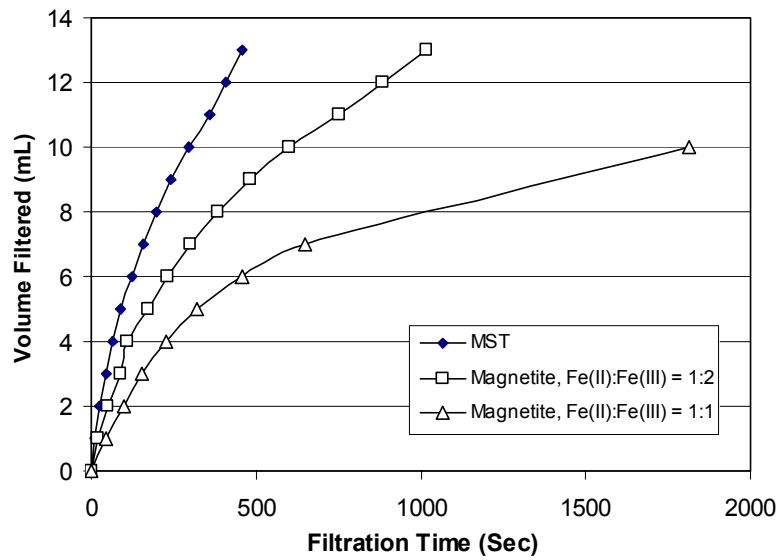


Figure 14. Filtration Studies Using 0.45-µm Nylon Membrane Filter at 2.2 g Fe or MST/L

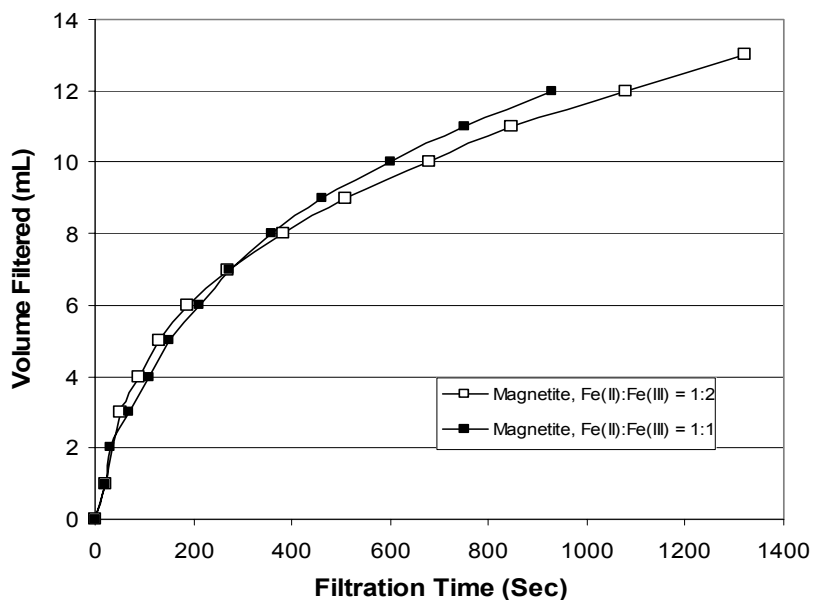


Figure 15. Filtration Studies Using 0.45- μ m PVDF Membrane Filter at 2.2 g Fe/L

Finally, the effect of temperature on magnetite particles agglomeration was checked in one limited study. When nylon filters with pore size of 20- or 40- μ m were used, it was visually observed that many of the magnetite particles passed through the filter membrane. This is to be expected based on the size distribution of the magnetite particles. However, when magnetite was formed at 45 °C in the solution and then stored overnight at that temperature, it was observed that it took a longer time to filter the particles and the particles were visually observed to be retained by the membrane.

III. FUTURE STUDIES

Through this study, we were able to provide a preliminary proof-of-concept for the use of in situ formed magnetite for the removal of Sr and actinides from SRS tank waste simulant. A number of additional studies are needed before this new process can be applied at SRS for tank waste treatment. These include:

A. Scale-up tests: The tests done so far (both DF and filtration tests) were performed using test-tube-scale volumes. However, factors such as mixing time, mixing intensity, and mixing pattern are known to affect the in situ formation of magnetite and ought to be tested. Beaker-scale and larger tests are needed to determine these effects in the scale up of the magnetite process.

B. DF tests with all isotopes in solution: The tests discussed in this work were performed using different combination of isotopes of interest that allowed the use of gamma and scintillation counting techniques. A verification of the magnetite performance will require performing additional DF tests with all isotopes of interest present in solution.

C. Tests using varying iron amounts: In almost all of the tests reported in this work, the maximum allowable amount of iron concentration, which is determined by the glass plant limitations, was used to provide the best case for proof-of-concept. Since the DF values obtained were much higher than the desired amount, there is room for reducing the amount of iron used while maintaining an acceptable DF performance. This possibility needs to be experimentally verified.

D. Additional filtration tests: It is not feasible to judge the magnetite filtration performance based on the preliminary tests made during this work under the one particular selection of filter media, temperature, and solids concentration that was used. The filtration tests done here were all that was feasible within the amount of funding and time available. There is a great need to define a series of representative filtration tests (including defining a suitable filter media, solids concentration, temperature, mixing time and intensity,... etc.), which will give a better evaluation of the relative performance of magnetite and MST, and which will be more directly correlated to the conditions prevailing in the X-flow filter process. Additionally, the filtration process is influenced, to a great extent, by the presence of the solids from the sludge, which also need to be filtered. This has to be taken into consideration when designing additional filtration tests.

E. Decontamination reversibility tests: There is a need to perform a series of tests to verify that the removal of the radionuclides by magnetite is irreversible, or minimally so, especially during the filtration and solid wash steps.

F. Real waste test: There is a definite need to perform a proof-of-concept test for the magnetite process using real tank waste solution. This will allow a check for any interferences caused by waste constituents which are not present in the simulant.

V. SUMMARY

In this work, we investigated some aspects of using in situ formed magnetite for the removal of Sr and actinides from SRS tank waste. The work was performed to study the feasibility of using magnetite as an alternative to the current MST technology, which suffers a number of technical and cost limitations. The experimental work was defined based on an operational envelope that was developed in collaboration with SRS. Waste simulant, prepared according to SRS' recipe, was used, with minor modifications to enable us to use the more accurate radiation counting techniques instead of ICP-MS. Decontamination of five radionuclides was measured. These radionuclides are Sr, Pu, Np, Am, and U. A very limited study was performed using Cs. In all DF tests, the maximum allowable iron concentration, as set by the operational envelope based on glass plant limitations for magnetite crystals, was used. This concentration is 2.2 g Fe/L and was based on the assumption that all the iron precipitate will be in the form of magnetite.

During the first phase of this work, we investigated the conditions for magnetite formation in the alkaline simulant solution. We found that the iron precipitate formed was actually a mixture of different iron compounds, including magnetite. There is evidence that the iron precipitate also includes ferric hydroxide, maghemite (Fe_2O_3), and possibly ferrous

hydroxide. A set of tests revealed that the amount of crystalline magnetite formed depends on the composition of iron solutions added, and the method of adding these solutions to the waste (all at once or drop wise). For simplicity purposes, this iron precipitate mixture was always referred to as “magnetite” throughout this work.

Decontamination tests gave excellent DF results for Sr, Pu(IV), and Np(V). DF values for Am and U(VI) were lower than the former three isotopes, but still within the process acceptable range. For all isotopes, DF values using magnetite were higher than those using MST, especially for Sr, Np, and Pu, where the magnetite DF values were almost 2 to 3 orders of magnitude higher than MST. The kinetics was also found to be excellent. Within 30 minutes of magnetite formation, DF values ranging from 130-850 were obtained for Np, Pu, and Sr, while the DF values were 2.4 and 1.5 for Am(III) and U(VI), respectively. Cesium removed using magnetite was minimal. After about 23 hours of magnetite formation, Cs DF values did not exceed 1.15.

A limited filtration study was performed to compare the filtration performance of magnetite particles to MST. A combination of gravity and vacuum filtration tests were performed utilizing a variety of filter media, including cellulose, nylon, PVDF, and polycarbonate. The tests revealed that magnetite filters faster than MST in the larger pore size filters (8 μm), whereas the opposite is true about the smaller filters (0.45 μm). This was attributed to the larger size of magnetite particles, measured during this study, which might have caused the blockage of the smaller filter pores. It was also concluded, based on the filtration results, that both filter material and temperature affect the filtration performance of magnetite. Additional tests are strongly recommended before conclusions could be made about the anticipated magnetite performance in a cross-flow filter setup, especially at conditions driven by the sludge solids in the tank.

Finally, a number of future studies are proposed at the conclusion of this report in order to provide a stronger basis for making a decision on using magnetite at SRS for waste treatment.

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APPENDIX A

SRS Recipe for Waste Simulant Preparation

PROCEDURE:

1. Prepare stock solution of Na₂CO₃ as indicated below.
2. In a 4L PE bottle, place approximately 2L of DDI H₂O and the Ultrex nitric acid.
3. Stir until well mixed and cool to room temperature.
4. Add the Al(NO₃)₃·9H₂O. Add U, Pu, Np and Sr-85.
5. Slowly add the 50 wt % NaOH solution with vigorous mixing until a white precipitate persists. Add the remainder of the NaOH solution rapidly with vigorous mixing.
6. Add the remainder of the salts followed by the Na₂CO₃ solution and mix for a minimum of 24 hours.
7. Filter through Whatman filter paper to remove undissolved solids. Limit exposure to air during filtration.
8. Store solution in tightly stoppered PE bottle labeled with name, date prepared, concentration and safety hazard warning after flushing vapor volume with nitrogen or argon.

Final Soln Vol (L) =	4.0	Soln Conc (M)
	Free NaOH	1.33E+00
	Total NaNO ₃	2.60E+00
	NaAl(OH) ₄	4.29E-01
	NaNO ₂	1.34E-01
	Na ₂ SO ₄	5.21E-01
	Na ₂ CO ₃	2.60E-02
	Total Na	5.6

Preparation of Na₂CO₃ Solution

(prepare 10% excess of amount needed to allow for filtration losses)

	MW (g/mole)	Qty (moles)	Salt Wt. (grams)	Meas. Wt. (grams)	Manufacturer	Lot #
Na ₂ CO ₃ ·H ₂ O	124.01	1.14E-01	14.19			

1. Dissolve indicated amount of Na₂CO₃ in 100 grams of DDI water. Record weight of salt and water used.
2. Mix until all solids have dissolved. Add more water if necessary. Record weight of any additional water used.
3. Add 2.0 g of MST slurry (Optima Lot # 33407 to bottle and mix at ambient laboratory temperature for a minimum of 48 hours. Record lot # and quantity of MST used
4. Filter suspension through 0.45 micron disposable filter and store filtrate in clean PE bottle labeled as follows.

Sodium Carbonate Solution
Treated with MST to Remove Tramp Sr
Date Prepared: mm/dd/yy

APPENDIX B

Radionuclides Preparation and Purification

Pu stock solution was purified by first oxidizing the plutonium to dissolve any Pu(IV) polymer, which could have been formed in the stock during storage. A calculated amount of the solution was evaporated in an Erlenmeyer flask twice with ~5 mL of concentrated nitric and perchloric acids until formation of the wet precipitate. The precipitate was dissolved in 7.5 M HNO₃ and Pu(VI), obtained as a product of oxidation, was reduced to Pu(IV) by an excess of hydrogen peroxide at ~ 50 °C. The solution was fed onto an ion exchange column containing Reillex™ HPQ anion exchanger in NO₃⁻ form, pretreated with 7.5 M HNO₃. Plutonium sorbs onto the anion exchanger as Pu(NO₃)₆²⁻, but all cations such as Am(III) and the bulk of UO₂²⁺, go through the column with nitric acid wash solution. Pu(IV) was desorbed with preheated 0.3 M HNO₃ solution and analyzed by gamma- and alpha spectroscopy. Neither Am nor Np were found in the gamma spectrum. However, there were two peaks in alpha spectrum that were assigned to Pu-239/240 (major peak) and Pu-238 (minor peak). A sample of the solution was submitted for ICP-MS analysis, which confirmed the presence of three Pu isotopes. The concentration of nitric acid in the Pu stock was increased up to 1.5 M HNO₃ to avoid formation of Pu(IV) polymer or Pu(IV) disproportionation. Electron absorption spectroscopy was applied to verify Pu tetravalent oxidation state.

To determine plutonium concentration in the stock, an aliquot was evaporated with a few drops of concentrated HClO₄ to oxidize Pu(IV) to Pu(VI), then the precipitate was dissolved in 1 M HClO₄, and transferred to a volumetric flask. An electron absorption spectrum was collected and the band at 830.4 nm ($\epsilon=550$ L/mol·cm) was used to calculate Pu concentration.

Np-237 stock was analyzed by gamma spectroscopy. A peak at 59.6 keV was assigned to Am-241, two less intensive peaks at ~17 and 20 keV were assigned to either Am-241 or Pu-238. All other peaks were assigned to Np-237 and its daughter isotope Pa-233.

Anion exchange method was applied to separate Np from Am and Pu. For this, the stock solution was evaporated with the mixture of concentrated nitric and perchloric acids until Np(VI) wet salts formation, then the precipitate was dissolved in ~7.5 M HCl. Np was reduced by hydrogen peroxide to tetravalent oxidation state to form NpCl₆²⁻. The completeness of the Np reduction was confirmed by electron absorption spectroscopy. No peak at 980 nm (Np(V)) was found in the optical spectrum.

The solution was fed on the column loaded with AGMP-1. The sorbent was previously washed with H₂O and then with 7.5 M HCl. After Np sorption, the column was washed with about 5 free bed volumes of 7.5 M HCl + 0.1 M HI solution at flow rate about 2 mL/min. Iodide is considered to be a very effective reducing agent for the reduction of Pu(IV) to Pu(III). Pu(III) is not sorbed by anion exchange resin, and should be removed by the wash solution. The most stable oxidation state for Am under these conditions is also 3+, therefore it should be washed out from the column, too.

After washing, Np was stripped by a preheated (70 °C) solution of 0.3 M HCl and analyzed by gamma spectroscopy. No Am-241 was found in the sample. However, alpha energy spectrum, collected to verify the stock solution purity, revealed two major peaks of equal intensities, which were assigned to Np-237 and Pu-238.

To separate Np and Pu, the above procedure was repeated, except 7.5 M HCl+1M HI solution was used to reduce and to wash Pu from the column. The alpha spectroscopy showed that about 99% of alpha activity of the stock solution is due to Np-237 decay, and 1% is due to Pu-238, which should be considered acceptable for our purpose. This method has a significant disadvantage, though. Iodide ions displace the neptunium hexachloro anions from the resin due to much higher K_d values, so large amount of the sorbent should be used to prevent Np loss during the process.

Another fraction of the stock solution was purified using Reillex™ anion exchange resin. For this, Np(IV) was sorbed onto the column as a $\text{Np}(\text{NO}_3)_6^{2-}$ anion complex from 7.5 M HNO_3 . The column was washed by 10 bed volumes of 7.5 M HNO_3 +0.3 M N_2H_4 + 2 g/L hydroquinone to separate Pu(III) from Np(IV). The Np was stripped by the preheated 0.4 M HNO_3 solution and analyzed by alpha spectroscopy. At least 99.5 % purity by alpha activity was achieved. The weight fraction of Pu-238 in the stock is less than 0.001%. This stock solution has been used for our experiments.

The Am-241 stock used in these experiments originated as a nitric acid solution. The stock was filtered through a 0.02 micron aluminum oxide membrane filter before addition to the simulant.

The Sr-85 stock used in these experiments began as a 0.1M HCl solution purchased from a vendor. No preparation of this solution was done before addition to the simulant.

The Np-239 stock was prepared from a stock of its parent nuclide, Am-243. The two isotopes were separated by a standard method to extract neptunium into triisooctylamine and strip with water.