The Application of In Situ Formed Mixed Iron Oxides in the Removal of Strontium and Actinides from Nuclear Tank Waste

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This article discusses the experimental program conducted at Argonne National Laboratory to study the performance of in situ formed mixed iron oxides (IS-MIO) for the removal of strontium (Sr), plutonium (Pu), neptunium (Np), uranium (U), and americium (Am) from the Savannah River Site (SRS) radioactive tank waste. The boundaries for the experimental work were defined in collaboration with SRS. IS-MIO was actually found to be a mixture of Fe(II) and Fe(III) oxides and hydroxides, including magnetite. Decontamination factor (DF) values were measured for both IS-MIO and monosodium titanate (MST), the baseline sorbent used by SRS. DF values for IS-MIO were found to be superior to MST for all isotopes studied. DF values for Pu, Np, and Sr, achieved within 30 min of IS-MIO 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. © 2010 American Institute of Chemical Engineers AIChE J, 56: 3012–3020, 2010
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Introduction

There are 144,000 m^3 (38 million gallons) of high-level waste stored in 49 tanks at the Savannah River Site (SRS) in South Carolina. This waste, which is a product of the Cold War era, contains a number of radioactive isotopes, including cesium (Cs), strontium (Sr), and actinide elements (including Np, U, Pu, and Am). The waste is composed of sludge (10%) and alkaline water-based supernate (90%). A portion of the supernate has transformed into a crystallized nitrate salt cake after the evaporation of water from the supernate.[1] It is expected that saltcake dissolution during waste processing will increase the overall waste volume from 144,000 to 303,000 m^3. In the accelerated approach[2]

for waste treatment, the sludge will be sent to the U.S. Department of Energy (DOE) Defense Waste Processing Facility (DWPF) for vitrification into borosilicate glass. The high-curie portion of the supernate will be processed in the Salt Waste Processing Facility, while the remaining low-curie supernate will either be treated for Sr and actinide removal within existing facilities or sent directly to the Saltstone Grout Facility at SRS for solidification, if its curie content was sufficiently low. Similar types of alkaline wastes containing actinides and fission-products are found at most other U.S. DOE sites and throughout the world, wherever reprocessing of spent fuel is performed or radionuclides are used in experimentation.

The baseline technology for Sr and actinides removal from the supernate is sorption by monosodium titanate (MST), followed by cross-flow filtration. Earlier results obtained at Savannah River National Laboratory showed that MST achieves adequate removal of Sr, Np, and Pu under equilibrium conditions.[3,4] These results, however, did not evaluate the kinetics of these reactions.[5,6] A following set of tests[7] showed slow kinetics for the decontamination of the

Table 1. SRS Waste Simulant Composition

Component	Solution Concentration (M)
Free NaOH	1.33
Total $NaNO_3$	2.60
$NaAl(OH)_4$	0.43
$NaNO_2$	0.13
Na_2SO_4	0.52
Na_2CO_3	0.026
Total Na	5.6

waste solution. Further studies[8,9] showed that high sodium concentration (7.5 M Na^+) in the waste solution caused slower sorption, requiring diluting the waste solution prior to processing. Based on these findings, the U.S. DOE judged this work inadequate to demonstrate the MST process for the decontamination goals.[10] Further, MST process testing in year 2000, using 0.2 and 0.4 kg MST/m^3 in a 5.6 M Na^+ waste,[11] indicated that Sr and Pu removal achieved the process goals under certain conditions, but Np decontamination goals were not achieved at either MST concentration. Hence, the MST process suffered from a significant drawback due to its low decontamination factor (DF) values and slow kinetics for actinides sorption. This opened the door for developing alternate sorbents or technologies. In situ formed mixed iron oxides (IS-MIO) was proposed by Argonne National Laboratory (Argonne) as an alternative to MST for the removal of Sr and actinides. IS-MIO is formed immediately in situ by adding solutions containing Fe(II) and Fe(III) ions to the alkaline medium. The IS-MIO 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. In the following phase, experimental work was performed to test the performance of the IS-MIO process. Eventually, many of the MST problems were resolved and MST is now being implemented at SRS. However, the use of the IS-MIO process will have uses in many decontamination efforts throughout the world.

Materials and Methods

An operational envelope was developed, which provided the experimental boundaries of the IS-MIO tests to follow. This includes identifying a suitable waste simulant composition, the concentrations and oxidation states of the radionuclides to be studied, the limit on the amount of iron added per liter of waste feed, and the DF requirements for the radionuclides to be tested. The boundaries of this operational envelope were decided upon after consultation with the key personnel at SRS. Following is a discussion on each of these elements.

Waste simulant composition

A recipe for the caustic waste simulant to be used in the experimental work was obtained from SRS.[12] The simulant composition is identical to that used by SRS in the baseline MST tests. This simulant was chosen, after discussions with SRS, for the following reasons:

(i) By using the same simulant that SRS used in their tests, a comparison could be established between the IS-MIO performance and that of MST.

(ii) This simulant composition provides high solubility of the actinides of interest, based largely on extensive studies of plutonium solubility. It is worth mentioning, however, that Pu concentrations in actual waste can greatly exceed its concentration in the simulant.

(iii) The simulant composition is reasonably close to the average composition of the actual tank waste.

(iv) This simulant was found to be stable after filtration (i.e., no salt precipitation) within a reasonable amount of time (up to few weeks).

Salt concentrations in the simulant are shown in Table 1. The detailed preparation procedure is provided elsewhere.[12]

IS-MIO and MST addition

Monosodium Titanate 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%. IS-MIO was formed in situ in the alkaline simulant by adding a mixture of Fe(II) and Fe(III) solutions to the simulant. This Fe(II)/(III) mixture solution was prepared by mixing known amounts of 1 M $Fe(NO_3)_3$ (in de-ionized (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) oxidizes to Fe(III). For example, when the $FeSO_4$ solution [before mixing with $Fe(NO_3)_3$] was stored for 5 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 (i.e., preformed) magnetite, purchased from Fischer Scientific Co.

Radionuclide concentrations and oxidation states in the waste simulant

In this work, focus was on the removal of Sr, Pu, U, Np, and Am from waste simulant. Isotopes with suitable half-lives were used to facilitate the concentration measurements. Table 2 shows the initial concentrations of the isotopes in the waste simulant and the oxidation states tested. These concentrations are similar to those tested at SRS, which helped establish a comparison to the MST process. It is worth mentioning that Pu(IV) behaves in similar fashion to Np(IV) from a precipitation standpoint and, therefore, was used as a surrogate for Np(IV). It is also worth mentioning that, while at SRS Am is not tested separately, the total alpha activity of the Pu/Am sample is monitored. Americium

Table 2. Concentrations and Oxidation States for Radionuclides Tested

Radionuclide	Solution Concentration	Oxidation State
Sr	0.1–0.6 mg/l*	II
Pu	0.2 mg/l	IV, VI
Np	0.5 mg/l	V, VI
U	10.0 mg/l†	VI
Am	Up to 0.2 mg/l	III

*Total Sr, including Sr-85 tracer.
†As uranyl nitrate hexahydrate.

Radionuclide	SRS DF Requirements (Average/Upper Bound)	ARGONNE DF Requirements for IS-MIO Process*
Sr	1/5.1	6
Pu/Am	12/49	50
Np	1/2	3
U	1/1	3

DF, decontamination factor.
*Identified as a goal DF values by ARGONNE team.

is believed to be present at trace concentration in these samples.

Decontamination factor requirements and its measurement

Decontamination factor is defined as the initial radionuclide concentration in the solution divided by its final concentration after treatment. The targeted DF values for this work were based on the needs identified by SRS.[13] SRS has performance requirements for the final concentrations of Sr and total alpha in solution. The current limits are 120 nCi/g for ^{90}Sr and ^{90}Y and 20 nCi/g for total alpha. To quantify the removal requirements for the individual isotopes, based on the overall performance requirements, SRS has defined two DF values for all radionuclides of interest, "average DF" and "upper bound DF".[13] These are listed in Table 3. The upper bound DF values were used as guidance to determine the minimum DF values for our tests, which are also listed in Table 3, as the "ARGONNE DF" requirement. Initially, it was decided that for the IS-MIO process to be judged successful, it should achieve at least the upper bound DF value set by SRS for all radionuclides tested. However, after consultation with SRS personnel, they indicated that the IS-MIO process would be considered a viable alternative if it achieves Pu DF > 12, and if it is filtered out of solution more easily than MST.

DF tests for radioisotopes removal by both IS-MIO and MST were performed to allow the comparison of IS-MIO and MST performance under identical conditions. The tests were done as follows. A predetermined 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, IS-MIO precipitates formed immediately upon addition to the simulant. The tubes were then placed on a rotating shaker. At predetermined 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. DFs were calculated by dividing the initial isotope concentration by its final concentration in solution after treatment.

All the DF tests involving iron were performed using 2.2 kg Fe/m^3, as specified in the following section. The maximum iron concentration was chosen to provide the best case for a

proof-of-concept for the IS-MIO process. DF tests using MST were less straightforward. As 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 as it could change the properties of hydrated MST particles. As an alternative, the MST slurry was filtered, using a 5-μm polycarbonate filter membrane, followed by particle washing with DI water and refiltration. MST particles, accumulated on the filter membrane, were then collected, weighed, and added to the simulant to produce a 0.4 kg MST/m^3 simulant. A preweighed sample of the filtered MST was placed in a desiccator to determine its moisture content. After drying for 24 h 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 kg of dehydrated MST/m^3 simulant.

Amount of iron used

If the IS-MIO process were to be implemented at SRS, the effect of adding iron to the high-level waste (HLW) on the subsequent performance of the DWPF glass plant has not been sufficiently investigated. This was proposed as a future study, should the IS-MIO process prove to be promising for Sr and actinide removal. Nonetheless, based on discussions with Dr. John Plodinec (John Plodinec, personal communication, 2002), from Mississippi State University, and Sam Fink and Sharon Marra (personal communications, 2002), from SRS, some potential impacts of the presence of iron in the glass plant feed were identified. The primary impact is that, although typical waste glass compositions can dissolve significant quantities of iron oxide, if the iron is in the form of magnetite its dissolution in glass is very slow. This can lead to a competition between the rate of dissolution and the sedimentation velocity of these particles. If magnetite particles accumulate in the melter, the magnetite layer at the bottom of the melter interferes with normal current flow, leading to reduced melt rates and eventually to failure of the melter. There are two key ways to solve this problem; the amount of magnetite is to be limited to 2% of the total iron content in the glass, which averages about 11–15 wt % of the glass weight (Sharon Marra, SRS, personal communication, 2002), or the size of the magnetite particles has to be controlled, as smaller particles dissolve more easily in the melter.

Based on preliminary material balance calculations, performed by SRS (Sam Fink, SRS, personal communication, 2002), the maximum amount of iron added to the waste solution, as a result of the IS-MIO process, will be 2.2 kg Fe/m^3 of waste. This value was obtained based on the flowsheet for the In-Tank Precipitation process, which shows an iron flow rate of 8.73 kg/h to the glass plant. Assuming 2% of that value, the iron feed rate can be up to 0.174 kg Fe/h. Hence, if all the iron added to the solution was converted to magnetite, the maximum amount of iron to be used is 3.04 kg magnetite/m^3 of solution.

Characterization of the formed iron oxides mixture

Precipitation tests were performed to determine the optimal conditions for IS-MIO formation. Tests were performed

Table 4. Effect of Different Parameters on IS-MIO Formation in SRS Waste Simulant

Test No.	Iron* 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 min
7	7.3	Green to black	Negligible	Y	Fe(III) added as Fe$_2$(SO$_4$)$_3$ instead of Fe(NO$_3$)$_3$

*Added as a 1:2 mix of FeSO$_4$ and Fe(NO$_3$)$_3$.

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$_4$Cl solution until the pH of the wash reached seven. 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° to 75° in two theta. The step size was 0.03° and the scan speed was 1.5°/min. Patterns were interpreted by comparison with International Center for Diffraction Data powder patterns. Particle size distribution of the iron oxide 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 kg Fe/m^3 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), with effective measuring range is from 1 to 1000 μm.

Results and Discussion

Iron oxides formation

Seven tests were performed to investigate the effects of different operating parameters on iron oxides 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 4. 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 4 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 4, several observations can be made about IS-MIO 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$_2$O$_3$), 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.

Table 5. Effect of Different Parameters on IS-MIO Formation in NaOH Solution

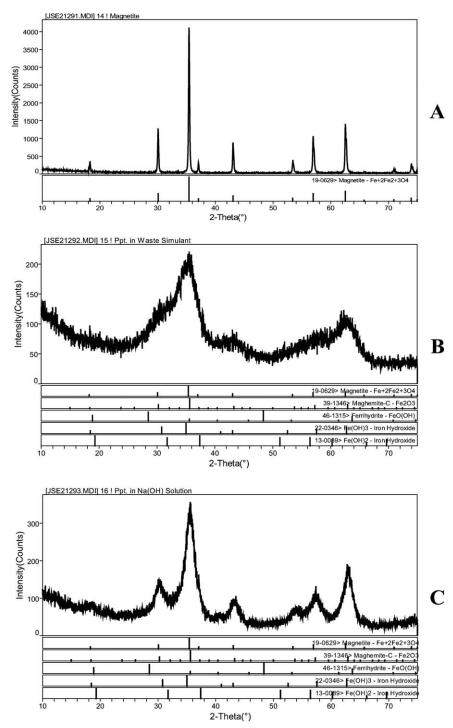| Test No.	Iron Concentration (mg Fe/ml)	NaOH Concentration (M)	Precipitate Color	Precipitate Response to Magnet	Fe(OH)$_3$ Layer? (Y/N)	Notes
1	7.3	6	Black	Strong	N	–
2	7.3	1	Green to black	Strong	N	–
3	7.3	2	Black	Strong	N	–
4	7.3	4	Black	Strong	N	–
5	7.3	6	Black	Weak to strong	N	Response to magnet 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 min

Figure 1. XRD patterns for formed iron oxides (A) commercial (preformed) magnetite, (B) iron oxides formed in situ in waste simulant, and (C) iron oxides formed in situ in NaOH solution.

Second, a number of changes led to the formation of Fe(OH)$_3$. These changes are adding the iron solution slowly (drop-wise) to the simulant, adding Fe(II) in water instead of the 0.5 M H$_2$SO$_4$ solution, and adding Fe(III) as ferric sulfate instead of ferric nitrate. It is not fully understood yet why these changes affect IS-MIO formation. An eighth test was performed (not shown in Table 4) 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, 5:1, and 1:1. 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 iron oxide formation, some precipitation tests were performed using NaOH solution (at 5.6 M Na$^+$ concentration) instead of the simulant. The outcome of these tests is
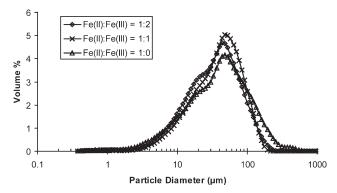
Figure 2. Particle size distribution of IS-MIO particles formed in waste stimulant.

Figure 3. Preliminary test to identify optimal Fe(II)/(III) ratio using Pu(IV) DF values.

summarized in Table 5. These results show that the precipitate's magnetic response is stronger in all cases than that formed in the SRS simulant, which indicates greater magnetite formation. This is also supported by the absence of any $Fe(OH)_3$ formation, as observed from the sixth column in Table 5. It is speculated that the presence of oxidizing agents, like the nitrate ion, are likely to affect magnetite formation. Three XRD tests were performed using commercial magnetite, iron oxides formed in situ in waste simulant, and iron oxides formed in situ in the NaOH solution. The XRD patterns for these three samples are shown in Figure 1A–C, 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 (Figure 1A). 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 (Figure 1C) shows peaks that are more defined and less broad than those for the simulant (Figure 1B). This is in agreement with the precipitation tests discussed earlier, which showed that more magnetite forms in NaOH solution than in the simulant.

Particle size distribution analysis was performed for IS-MIO 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 Figure 2. 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. It was observed that the IS-MIO 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.
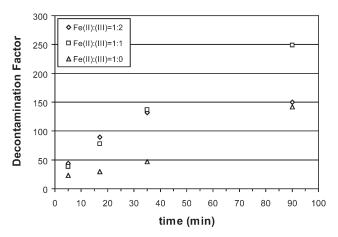
Sr and actinides removal using IS-MIO

Figure 3 shows the first set of DF tests for Pu(IV). This test went for a short time (1.5 h) and was intended to find the optimal Fe(II):Fe(III) ratio, in terms of DF results. The total iron concentration in solution in these tests was 2.2 kg Fe/m^3, which was the concentration used in all DF tests discussed in this section. As evident from Figure 3, 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. A second test was performed using commercial magnetite for Pu removal. DF results for this test are shown in Figure 4. Although DF values were still on the rise after 90 min of magnetite contact, these values were still very low (<1.2), which discouraged studying commercial magnetite any further and focusing instead on in situ formed iron oxides. The poor performance of commercial magnetite (Figure 4) compared to in situ formed iron oxides (Figure 3) gives some insight on the Pu removal mechanism. One possibility is that Pu ions are incorporated into the IS-
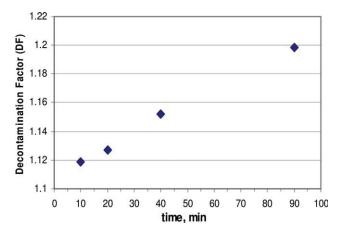

Figure 4. Pu (IV) removal using commercial (preformed) magnetite.

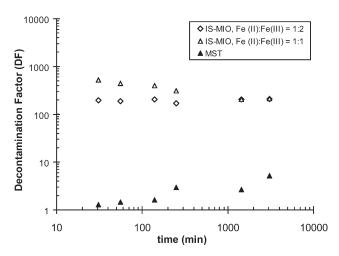[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5. Pu(IV) removal using IS-MIO.

Figure 7. Strontium (Sr) decontamination factors using IS-MIO and MST.

MIO structure as they form (i.e., co-precipitation mechanism). An alternative is that Pu is being removed by surface adsorption on the iron oxides surfaces. If this is the case, the results in Figure 3 strongly suggest that the formation method for IS-MIO has a strong effect on the available adsorption surface, where preformed magnetite has less adsorption capacity than the in situ formed oxides. This is so because commercial (preformed) magnetite is a crystalline material with a small surface area. The third possibility is that other iron precipitates, which co-precipitate with magnetite as they all form in situ, are the primary drive behind the removal.

A second test using IS-MIO for Pu (IV) removal was conducted and was extended to 48 h. Results for this test are shown in Figure 5, which shows that IS-MIO, which shows that IS MIO, formed using Fe(II)/(III) ratio of 1:2 or 1:1. achieves DF values two orders of magnitude higher than those achieved by MST. More importantly, these high DF values are achieved within 30 min of IS-MIO formation. After 30 min, 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 (DF = 49, Table 3). Another interesting observation is that iron solution with Fe(II)/(III) = 1:1 yielded higher DF values than
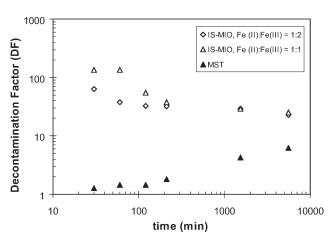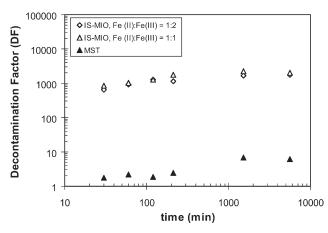
the solution with Fe(II)/(III) = 1:2. This was found to be the case for all radionuclides tested, as will be shown shortly.

DF values for Np(V) are shown in Figure 6. Similar to Pu(IV), DF values for IS-MIO are, by far, higher than those for MST and exceed the upper bound requirement set by SRS (DF = 2, Table 3). 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.

The highest DF values using IS-MIO were achieved for Sr. Figure 7 shows the change in DF values for Sr over a 93-h period using both IS-MIO and MST. DF values using IS-MIO were three orders of magnitude larger than those achieved using MST. DF values of about 1000 were obtained within 1 h of IS-MIO formation. The DF values then continued to rise over time and reached about 1800 within 4 h and about 2200 within 24 h. The current upper bound DF requirement for Sr is about six.

DF tests for Am(III) and U(VI) are shown in Figures 8 and 9, respectively. For both isotopes, the DF values achieved using IS-MIO 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
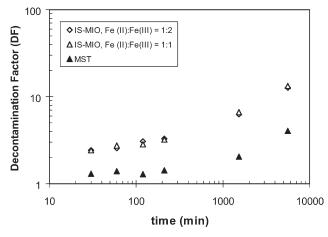

Figure 6. Np(V) removal using IS-MIO

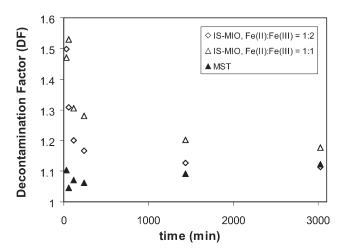Figure 8. Am(III) decontamination factors using IS-MIO and MST.

Figure 9. U(VI) decontamination factors using IS-MIO and MST.

about 2.5 in 30 min up to 7 in 24 h and then up to 13 within 93 h. 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 h to achieve higher DF values. Uranium tests using IS-MIO exhibited the lowest DF value of all radionuclides tested, achieving a DF value of 1.5 at 30 min. The DF then decreased to 1.3 in 4 h and then to 1.2 in 48 h, 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 (Sam Fink, SRS, personal communication, 2002). 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 DF 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.[14] 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.[15] 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 IS-MIO. 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.[16] 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 com-

plete, resulting in lower DF values for Np than for Pu(IV), but higher than U(VI).

Conclusions

Findings of this work indicate that IS-MIO can be used effectively for the removal of strontium (Sr) and key targeted actinides (Pu, Np, Am, and U) from the SRS radioactive tank waste, which can enable the separation of tank waste into high- and low-level waste streams, allowing optimized further processing. The amount of iron to be added was based on an operational envelope established in consultation with SRS, to ensure that the iron does not interfere with the subsequent waste processing steps. The waste simulant used in this study was similar to that used by SRS for their tests, and was prepared according to their recipe. The performance of IS-MIO was found to be superior to that of the current baseline sorbent, MST, as the amounts of radionuclides removed by IS-MIO were much larger than those removed by MST, reaching orders of magnitude difference in some cases. For all isotopes tested, the DF exceeded, by far, the requirements set by DOE. This means that a more effective waste separation can be achieved using IS-MIO than by MST. The best performance, in terms of waste decontamination, was observed for Sr and Pu, followed by Np.

Several tests were also conducted to identify the optimal Fe(II):Fe(III) ratio to be used when forming the IS-MIO. This ratio was found to be 1:1 and 1:2. Additional testing has also revealed that the iron oxides/hydroxides have to be formed in situ within the waste liquid itself to achieve the best performance and that commercial magnetite formed ex situ did not perform as well. Further testing will be needed to investigate the implications of applying the IS-MIO process on the other stages of waste processing, especially solids cross-flow filtration and HLW glass vitrification.

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