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Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Slater, S. A. , Chamberlain, D. B. , Aase, S. A. , Babcock, B. D. , Conner, C. , Sedlet, J. and Vandegrift, G. F.(1997) 'Optimization of Magnetite Carrier Precipitation Process for Plutonium Waste Reduction', Separation Science and Technology, 32: 1, 127 — 147

To link to this Article: DOI: 10.1080/01496399708003191

URL: http://dx.doi.org/10.1080/01496399708003191

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SEPARATION SCIENCE AND TECHNOLOGY, 32(1-4), pp. 127-147, 1997

OPTIMIZATION OF MAGNETITE CARRIER PRECIPITATION PROCESS FOR PLUTONIUM WASTE REDUCTION

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ABSTRACT

Transuranic (TRU) waste that is being generated at Argonne National Laboratory has a TRU activity ranging from 10^2 to 10^7 nCi/g with a wide variety of chemical compositions. Currently, the waste is stored in highly acidic solutions that must be neutralized for intermediate storage. A magnetite carrier precipitation process has been adapted to concentrate TRU isotopes in a noncorrosive solid phase. In this paper, we report the results of a series of laboratory tests done to optimize the process. The parameters we optimized included (1) magnetite concentration used to precipitate plutonium from solution, (2) formation of magnetite (*in situ* or *ex situ*), (3) processing pH, and (4) temperature and mixing time of the carrier precipitation. We also studied the effects of anions, cations, and complexing agents in the waste solutions on the carrier precipitation and the effect of magnetite solids loading on the filtration equipment. An overview is given of the planned full-scale process, which will be operated in a glovebox.

INTRODUCTION

Transuranic (TRU) waste generated at Argonne National Laboratory (ANL) is currently stored in highly acidic solutions, and it requires stabilization for long-term storage. Treatment of the liquid TRU waste would alleviate two problems associated with its intermediate storage: the high radionuclide inventory in the building and the limitation of storage space for liquid wastes. The Separation Science and Technology Section of the Chemical Technology and Waste Management Operations Divisions at ANL are jointly developing a process to treat this TRU waste. If a treatment process can produce a liquid supernatant that has an alpha activity of ≤ 0.1 nCi /mL (i.e., 1.51 μg ^{239}Pu/L), the supernatant can be sent to the ANL low-level waste (LLW) evaporator/concentrator system. The solid precipitate generated by this system will be packaged and transported to a long-term storage facility such as the Waste Isolation Pilot Plant. After reviewing available methods for removing TRUs from solution, we chose magnetite carrier precipitation for laboratory-scale testing because it is simple, robust, and operable in a glovebox [1]. This magnetite carrier precipitation process is based on work done at Rocky Flats [2, 3, 4, 5]. The goal of the laboratory tests was to optimize the operating parameters of the magnetite carrier precipitation process. The parameters we optimized included (1) magnetite concentration used to precipitate plutonium from solution, (2) formation of magnetite (*in situ* or *ex situ*), (3) processing pH, and (4) temperature and mixing time of the carrier precipitation. We also studied the effects of anions, cations, and complexing agents in the waste solutions on the carrier precipitation and the effect of solids loading on the filtration equipment. On the basis of this testing, we have designed a full-scale process, which is operated in a glovebox, for treating ANL TRU waste solutions.

CARRIER PRECIPITATION PROCESS

Figure 1 gives a schematic of the full-scale magnetite carrier precipitation process being implemented at ANL. The full-scale process was designed based on the results from the optimization tests. The waste will be treated in a glovebox equipped to handle radioactive wastes because the TRU activity of the waste solutions is in the range of 10^2 to 10^7 nCi/mL. To begin the treatment process, several wastes originally stored in small

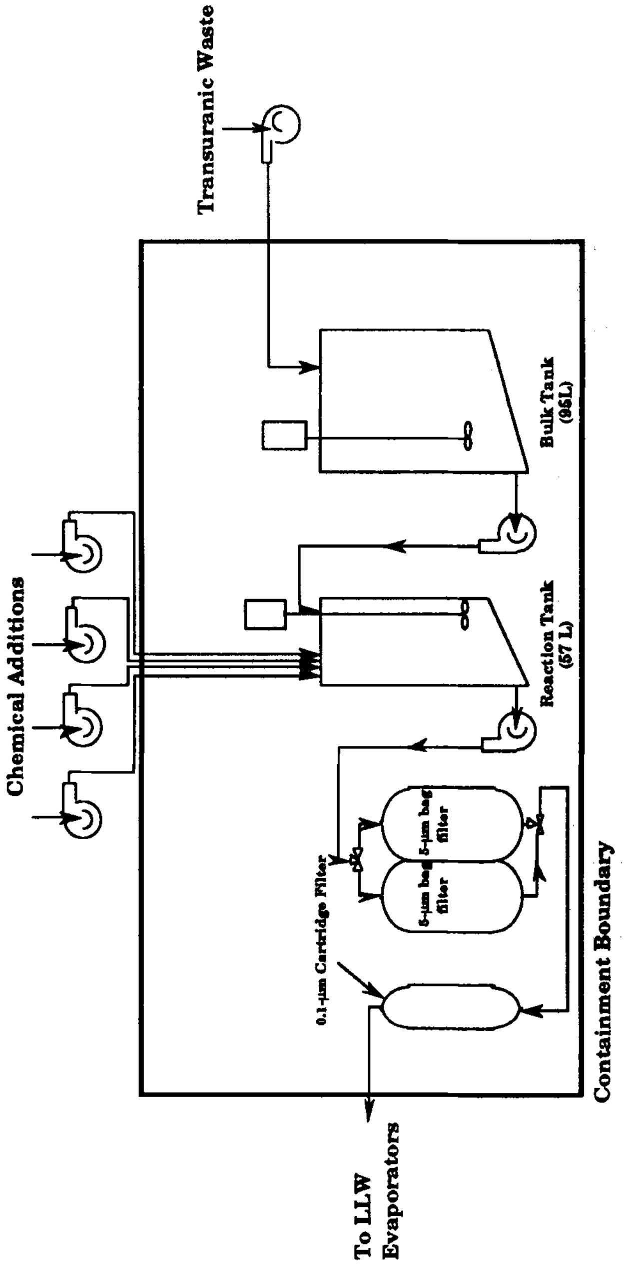

Fig. 1. Radioactive Glovebox Setup for the Planned Full-Scale Magnetite Carrier Precipitation Process.

containers (0.5 to 25 L) are combined. The wastes are mixed, a sample is taken, and the alpha activity is measured using liquid scintillation counting. The chemical composition of the waste may also need to be determined because the waste requisitions filed by the waste generators may be inaccurate. Next, the waste is pumped from the bulk tank to the reaction tank. In the reaction tank, 6M sodium hydroxide is added until a pH of 12 is reached. A control system maintains a pH of 12 in the reaction tank. To form the magnetite, a solution of 1M ferric nitrate and 0.5M ferrous sulfate in 0.5M sulfuric acid solution is added to the reaction tank.[1] Magnetite forms in the reaction tank immediately upon addition of the ferric and ferrous solutions. After the solution is mixed for a minimum of 30 min, the solution from the reaction tank is sent to the filters to separate the liquid supernatant and the solid precipitate. The supernatant is sent to the low-level waste evaporator/concentrator system, which is currently installed in the ANL Waste Management facilities. The precipitate is concentrated in 5-μm bag filters and a 0.1-μm cartridge filter. The filters containing the precipitate are packaged so they may be sent to a long-term storage facility, such as the Waste Isolation Pilot Plant [1].

OPTIMIZING PROCESS PARAMETERS

Our TRU waste treatment system is designed to concentrate the transuranics in the solid precipitate and to produce a supernatant with an alpha activity ≤0.1 nCi/mL (i.e., 1.5 μg ^{239}Pu/L). The 0.1 nCi/mL limit is based on the operating constraints of ANL Waste Management Operations LLW evaporator/concentrator system. The only transuranic element discussed here is plutonium. We have done initial tests for other transuranics (Np and Am), but those tests will be discussed in future publications.

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[1] The Fe^{3+}:Fe^{2+} mole ratio was varied from 1:1 to 3:1 with no significant changes in the formation or carrying ability of the magnetite.

In developing a magnetite carrier precipitation process to treat TRU waste, we studied the following parameters: magnetite concentration; magnetite formation; process pH; temperature; mixing time; effects of anions, cations, and complexing agents; and filtration. In this section, we discuss the general approaches used to test these parameters.

Magnetite concentration

In the waste treatment process described here, magnetite is used to carry plutonium from the waste solutions. To maximize decontamination of the waste solution while minimizing the formation of solids, the magnetite concentration must be optimized. To do this, we first performed test-tube-scale experiments (5 to 10 mL) and then beaker-scale experiments (50 to 150 mL) at various magnetite concentrations. The actual TRU waste treatment process that will be used at ANL is approximately 200 times the scale of the beaker-scale test.

Magnetite formation

In a magnetite carrier precipitation process, magnetite can be formed *in situ* or *ex situ*. In an *in situ* process, the ferric/ferrous solutions are added directly to the reaction tank to form magnetite. In an *ex situ* process, magnetite is first formed as a slurry and then added to the reaction tank. When magnetite is formed *in situ*, the carrier precipitation can be done in either a direct-strike or a reverse-strike sequence. In a direct-strike sequence, the ferric/ferrous solution is added to the acidic waste first, followed by the sodium hydroxide. In a reverse-strike sequence, the sodium hydroxide is added first, then the ferrous/ferric solution is added to form the magnetite. Both *in situ* and *ex situ* magnetite formation were evaluated to determine the most effective process over a wide range of waste compositions. (Note: In our experiments, magnetite was formed similarly to that done by researchers at Rocky Flats [3]. The appearance of our precipitate was black and was responsive to a magnetic field; however, methods such as X-ray diffraction were not employed to verify that the precipitate was indeed magnetite (Fe_3O_4).)

Process pH

For our TRU waste treatment process, the pH will be maintained by using a pH controller. Controlling the pH during processing is important in carrier precipitation, since the pH of a solution strongly influences the extent of carrying [6]. In the studies reported here, the solution pH values were varied in the alkaline region.

Temperature and mixing time

Both temperature and mixing time can affect the rate of a carrier precipitation process. Furthermore, increasing the mixing time will generate a precipitate with a larger particle size. In separate tests, the temperature was elevated and the mixing time was varied.

Effects of anions, cations, and complexing agents

Anions, cations, and complexing agents in waste solutions can hinder carrier precipitation processes, depending on the carrier and the composition of the waste solution, by inhibiting either the formation of magnetite or the carrying of TRU elements, or both [2]. The wastes to be treated at ANL vary in composition; therefore, we added a variety of anions, cations, and complexing agents to acid solutions to determine how much they affected the carrying of plutonium during carrier precipitation.

Filtration

After carrier precipitation is completed, the solid precipitate will be separated from the liquid supernatant by filtration through a series of two 5-μm bag filters and a 0.1-μm cartridge filter. To optimize the filtration step, we needed to determine the amount of solids that could be loaded on the filter before its pressure limit was exceeded. Beaker-scale tests were done by pumping a suspension through a small disc membrane filter and measuring the pressure drop. The filters for the actual ANL TRU waste treatment process are approximately 140 times the scale of the beaker-scale filtration tests.

EXPERIMENTAL

For the magnetite carrier precipitation tests, a simulated waste solution was prepared, which consisted of 1M HNO_3 and a ^{239}Pu tracer. The simulated waste solution used in these experiments adequately represents the wastes to be treated in the ANL waste treatment process. Typical radioactive wastes to be treated in this process are aqueous, acidic, solutions which may contain metals, salts, or complexing agents [1]. Then, 6M NaOH was added to the initial solution until a pH of 12 was reached. Magnetite was formed *in situ* in the solution by adding 1M $Fe(NO_3)_3$ and 1M $FeSO_4$ in 0.5M H_2SO_4 in a 2:1 Fe^{3+}:Fe^{2+} mole ratio. The volume of ferric and ferrous solutions added depended on the concentration of magnetite desired. After all additions, the final solution was mixed for 5 to 10 min for the test-tube-scale experiments and 30 min for the beaker-scale experiments. The liquid supernatant and the solid precipitate were centrifuged and separated. The supernatant was recovered, and its alpha activity was counted by a Packard 2200CA TRICARB liquid scintillation analyzer. The solid precipitate was dissolved in concentrated nitric acid by heating to a vigorous boil. A volume of 200 µL of concentrated phosphoric acid and 3 mL of deionized water were added to the dissolved precipitate to make the solution colorless for efficient counting of the alpha activity. The alpha activity of the dissolved precipitate was counted to calculate a material balance for each experiment. After material balances of 100±5% were achieved consistently, counting of the precipitate activity was discontinued.

For the filtration tests, magnetite solutions containing 10% solids were pumped through a small disc membrane filter to determine the solids loading and the corresponding pressure drop across the filter. A volume of 150 mL of magnetite solution was pumped through a 5-µm filter at a flow rate of 27.3 mL/min. The filter had a surface area of 17.4 cm^2. Periodically throughout the test, the pressure drop was measured with an Omega pressure transmitter (Model PX216-060AI).

RESULTS AND DISCUSSION

Analysis

In optimizing the magnetite carrier precipitation process, two factors were calculated: the final plutonium concentration of the solution and the decontamination factor (DF). The DF is defined as:

$$\text{decontamination factor (DF)} = \frac{\text{initial plutonium concentration}}{\text{final plutonium concentration}} \qquad (1)$$

These concentrations are for the initial and final solutions: the initial solution is the solution before the addition of sodium hydroxide and ferric/ferrous solution; the final solution is the solution (supernatant) after all additions have been completed and the precipitated solids have been removed by centrifugation or filtration. For our experiments, a final plutonium concentration of ≤1.51 μg/L and ^{239}Pu DF values $\geq 10^4$ were considered successful. It was determined, based on error analysis and estimation of carry-over error, that DF uncertainties of about ±10% are not significantly different.

The variation observed in the ^{239}Pu DF may have arisen for the following reasons: variation in the initial plutonium concentrations, inefficiency of centrifuging the suspension to separate the supernatant and the precipitate, and variation in individual methods of the different researchers who performed the tests. The differences between the beaker-scale tests and the test-tube-scale tests indicate that the beaker-scale tests better simulated the magnetite carrier precipitation process.

Magnetite Concentration

The goal in optimizing the magnetite concentration was to achieve a sufficiently low plutonium concentration in the supernatant while minimizing the formation of solids. Figure 2 illustrates the effect of varying magnetite concentration on the ^{239}Pu DF. For both the test-tube-

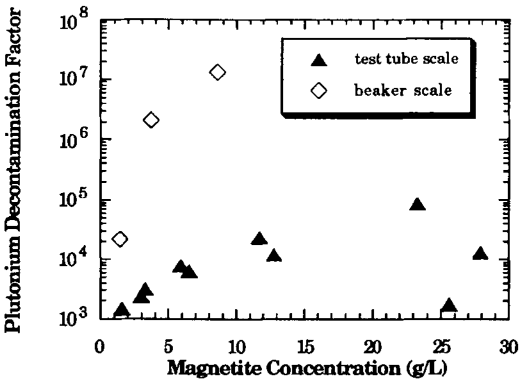

Fig. 2. Effect of Varying Magnetite Concentration on the ^{239}Pu DF.

scale and the beaker-scale experiments, we used magnetite formed *in situ* in a reverse-strike carrier precipitation. For the test-tube-scale experiments, no pH controller was used, and the supernatant was centrifuged only; however, for the beaker-scale tests, a pH controller maintained a pH of approximately 11.5, and the supernatant was filtered through a 0.1-μm syringe filter. These conditions were used to simulate the planned full-scale waste treatment process. The magnetite concentration used ranged from 1.3 to 27.8 g/L.

Beaker-scale measurements achieved higher ^{239}Pu DF values than the test-tube-scale measurements. All the beaker-scale tests achieved ^{239}Pu DF values greater than 10^4 (magnetite concentrations were 1.3, 3.6, and 8.5 g/L). Boyd et al. were able to achieve DF values in the range of 10^4 using 2 g/L magnetite and a magnetic separator [3]. The test-tube-scale tests achieved ^{239}Pu DF values greater than 10^4 only for magnetite concentrations greater than 11.6 g/L, with one exception. At 25.5 g/L, the DF dropped substantially because the final solution was acidic (pH ≈ 3). No apparent explanation can be given for the drop in the DF at 27.8 g/L. The difference between the beaker-scale and test-tube-scale tests, which differed in methods of pH control and separation, shows that both pH and filtration will affect the optimization of magnetite concentration.

Magnetite Formation

A comparison was done to determine whether *in situ* or *ex situ* magnetite carrier precipitation is more efficient in removing plutonium from the waste solution. Figure 3 presents the comparison of the plutonium decontamination factor for *in situ* and *ex situ* magnetite formation as a function of magnetite concentration. In both sets of tests, we used a reverse-strike carrier precipitation. As shown in Fig. 3, magnetite formed *in situ* achieved higher decontamination factors than magnetite formed *ex situ* at magnetite concentrations higher than 5.8 g/L.

This result suggests that there may be two mechanisms involved in removing plutonium from waste solutions using magnetite carrier precipitation: adsorption of plutonium onto the magnetite surface or chemical substitution of plutonium into the magnetite matrix. Also, since Pu (III) is the least soluble species of plutonium, the higher decontamination factors for the *in situ* formed magnetite may be explained by the reduction of Pu (V) to Pu (IV) and the reduction of Pu (IV) to Pu (III) by Fe (II) [7]; furthermore, trivalent actinide hydroxides precipitate out of solution completely at a pH greater than 10 [8]. In the waste solutions there may be compounds, such as phosphates, that complex with iron and may prevent or hinder magnetite formation [2]. In such instances, the process that should be implemented is carrier precipitation with magnetite formed *ex situ*.

We have observed that in the direct-strike carrier precipitation process, ferric hydroxide was usually formed instead of magnetite. Although ferric hydroxide has also been used for precipitating transuranics from solution, it is not as efficient as magnetite carrier precipitation [9]. Magnetite carrier precipitation is able to achieve improved solid/liquid separation and higher decontamination factors than ferric hydroxide precipitation [10]. Therefore, for greatest efficiency, magnetite should be formed in a reverse-strike process.

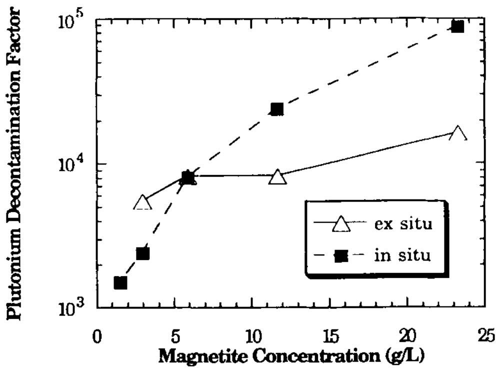

Fig. 3. Comparison of ^{239}Pu DF for *In Situ* and *Ex Situ* Magnetite Formation as a Function of Magnetite Concentration.

Process pH

An optimum processing pH was determined by treating four simulated waste solutions having pH values of 8, 10, 12, and 14. The magnetite was formed *ex situ* to avoid altering the pH of the solution. The magnetite concentration used for each experiment was 12.4 g/L and the initial plutonium concentration was 1.93E-2 g/L. The results are given in Fig. 4.

Magnetite carrier precipitation performed at a pH of 12 achieved a ^{239}Pu DF of 1.47E+4, which agrees with similar tests done by Kochen [4]. Kochen determined that the optimum pH range for removing plutonium from solution is between 12 and 13; if the pH is below 11.5 or above 13.5, plutonium removal is decreased [4].

Temperature and Mixing Time

The temperature and the mixing time were varied to determine their effects on the carrier precipitation process. Magnetite carrier precipitation experiments were performed at 25°C and 70°C. These experiments were

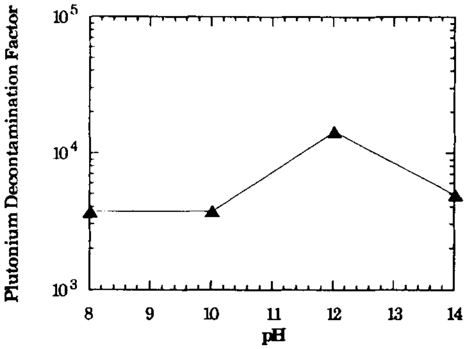

Fig. 4. Effect of Varying pH on the ^{239}Pu DF.

done at test-tube-scale with *in situ*-formed magnetite and reverse-strike carrier precipitation.

The results presented in Table 1 suggest that increasing the processing temperature by 45°C does not significantly increase the efficiency of the magnetite carrier precipitation process. Both experiments done at room temperature (25°C) met the processing goal of DF>10^4; one achieved a final ^{239}Pu concentration below the goal of 1.51E-6 g/L. The concentration reached in the other room temperature experiment, 1.63E-6 g/L, is not significantly different from the goal (<10% difference). Therefore, processing the transuranic waste solutions at elevated temperatures is unnecessary.

In another series of experiments, the mixing time was varied: the solutions were mixed for 5, 30, 60, 120, or 180 min. Table 2 presents the results. These experiments were done at test-tube scale (except where noted) with *in situ*-formed magnetite and reverse-strike carrier precipitation.

These results show that varying the mixing time does not affect the magnetite carrier precipitation. However, for the beaker-scale tests at an

Table 1. Effect of Temperature on the Final ^{239}Pu Concentration and ^{239}Pu DF.[a,b]

Temperature (°C)	Final ^{239}Pu Conc. (g/L)	^{239}Pu DF
25	1.63E-6	1.59E+4
25	3.11E-7	8.33E+4
70	1.63E-7	1.59E+5
70	2.13E-7	1.22E+5

[a] Magnetite concentration = 12.2 g/L.
[b] Initial ^{239}Pu concentration = 2.59E-2 g/L.

Table 2. Effect of Mixing Time on the Final ^{239}Pu Concentration and ^{239}Pu DF.

Mixing Time (min)	Magnetite Conc. (g/L)	Initial ^{239}Pu Conc. (g/L)	Final ^{239}Pu Conc. (g/L)	^{239}Pu DF
5	14.8	1.54E-2	4.53E-8	3.40E+5
5[a]	8.7	1.63E+0	3.62E-5	4.50E+4
30	14.8	1.54E-2	1.21E-7	1.27E+5
60	14.8	1.54E-2	7.55E-8	2.04E+5
120[a]	8.7	1.63E+0	4.23E-5	3.85E+4
180[a]	8.7	1.63E+0	4.83E-5	3.37E+4

[a] Beaker scale experiment.

initial plutonium concentration of 1.63 g/L, the final plutonium concentration did not meet the 1.51E-6 g/L criterion for processing in the ANL low-level waste evaporator/concentrator system. In comparing the beaker-scale tests from Fig. 2 and Table 2, the DFs for the beaker-scale tests were higher in Fig. 2, which may be due to the fact that the Fig. 2 beaker-scale tests were pH controlled and the supernatant was filtered.

Other researchers have found that a reaction time of 10 min is sufficient to lower the concentration from 1E-4 to 1E-8 grams of plutonium per liter of solution in a magnetite precipitation process [5]. Another time issue must also be considered: aging of the solution. The effect of aging on plutonium retention by magnetite have been tested by Boyd et al.: in seven days, the final concentration increased from 1E-8 to 1E-5 grams of plutonium per liter of solution [5], indicating that the magnetite had lost significant adsorption capabilities. Therefore, precipitated solids should be filtered soon after treatment to prevent dissolution.

Anion Effect

To determine the effect of anions on the magnetite carrier precipitation process, different anions were added to the simulated waste solution. These experiments were done at test-tube-scale with *in situ*-formed magnetite and reverse-strike carrier precipitation. Table 3 shows the results.

The final plutonium concentrations are below the processing goal of 1.51E-6 g/L (^{239}Pu DF>10^4) with the exception of those for the phosphate tests. Phosphate anion interfered with the *in situ* formation of magnetite at magnetite concentrations of 13.4 and 14.8 g/L. These results agree with those of other researchers, who found that magnetite formation is typically unaffected by most anions [2]. If any anions present in the waste hinder *in situ* magnetite formation, the magnetite should be formed *ex situ*.

Cation Effect

To determine the effect of cations on the magnetite carrier precipitation process, different cations were added to the simulated waste solution. These experiments were done at beaker-scale with *in situ*-formed magnetite and reverse-strike carrier precipitation. Table 4 presents the results.

All the final plutonium concentrations are below the processing goal of 1.51E-6 g/L (^{239}Pu DF>10^4). This indicates that, at the cation concentrations studied, there are no cationic interferences with the

Table 3. Effect of Various Anions on the Final ^{239}Pu Concentration and ^{239}Pu DF.

Anion	Anion Conc. (g/L)	Magnetite Conc. (g/L)	Initial ^{239}Pu Conc. (g/L)	Final ^{239}Pu Conc. (g/L)	^{239}Pu DF
Cl^-	35	14.8	1.54E-2	1.66E-7	9.28E+4
Cl^-	35	24.0	1.02E-1	1.24E-7	8.23E+5
F^-	19	14.8	1.54E-2	6.80E-7	2.26E+4
NO_3^-	62	14.8	1.54E-2	3.02E-8	5.10E+5
NO_3^-	62	24.0	1.02E-1	7.28E-8	1.40E+6
SO_4^{2-}	48	14.8	1.54E-2	4.38E-7	3.52E+4
SO_4^{2-}	96	24.0	1.02E-1	1.74E-8	5.86E+6
PO_4^{3-}	95	13.4	1.54E-2	1.95E-5	7.90E+2
PO_4^{3-}	47.5	14.8	1.54E-2	1.63E-6	9.45E+3
PO_4^{3-}	95	24.0	1.02E-1	1.30E-9	7.85E+7

precipitation of plutonium. Also, the added cations did not hinder the *in situ* formation of magnetite. After the addition of sodium hydroxide, several of the cations formed gelatinous precipitates, which may make the solutions difficult to filter. These cations were Mg^{2+}, Cu^{2+}, Cd^{2+}, and La^{3+}. The simulated waste solution that contained Al^{3+} formed an aluminum hydroxide precipitate after the addition of sodium hydroxide; however, because aluminum is amphoteric, the precipitate quickly redissolved. The simulated waste solution that contained Ca^{2+} formed a calcium hydroxide precipitate; however, the suspension did not appear to be gelatinous, and filtering should not be difficult.

Simulated waste solutions that contained cations did not reduce the efficiency of magnetite carrier precipitation to remove plutonium from solution; however, these solutions did increase the amount of precipitate which was generated since the cations were precipitated as hydroxides from solution.

Table 4. Effect of Various Cations on the Final ^{239}Pu Concentration and ^{239}Pu DF.

Cation	Cation Conc. (g/L)	Magnetite Conc. (g/L)	Initial ^{239}Pu Conc. (g/L)	Final ^{239}Pu Conc. (g/L)	^{239}Pu DF
K^+	2.0	14.0	8.67E-3	2.93E-7	2.96E+4
K^+	52	14.0	1.29E-2	2.96E-7	4.36E+4
Li^+	50	13.3	7.73E-3	2.84E-7	2.72E+4
Na^+	2.1	14.1	8.79E-3	1.36E-7	6.46E+4
Na^+	58	12.0	6.45E-3	4.80E-8	1.34E+5
Ca^{2+}	24	14.2	8.98E-3	2.93E-8	3.06E+5
Cd^{2+}	71	12.6	7.02E-3	1.51E-8	4.65E+5
Cu^{2+}	190	14.8	1.54E-2	1.02E-7	1.51E+5
Mg^{2+}	20	13.0	7.43E-3	2.16E-8	3.44E+5
Zn^{2+}	2.2	14.5	9.33E-3	1.12E-7	8.33E+4
Al^{3+}	7.7	14.8	1.10E-2	1.13E-7	9.73E+4
Al^{3+}	20	16.3	1.21E-2	7.76E-8	1.56E+5
Ce^{3+}	2.2	14.1	9.36E-3	2.11E-8	4.44E+5
Cr^{3+}	1.9	14.1	7.16E-3	1.06E-7	6.75E+4
La^{3+}	2.2	14.5	9.36E-3	1.81E-8	5.17E+5
La^{3+}	20	14.2	8.98E-3	1.08E-8	8.31E+5
Zr^{4+}	2.0	13.1	7.58E-3	3.52E-8	2.15E+5

Complexing Agent Effect

To determine the effect of organic complexing agents on the magnetite carrier precipitation process, different complexing agents were added to the simulated waste solution. These experiments were done at test-tube-scale using *in situ*-formed magnetite (except where noted) in reverse-strike carrier precipitation.

Table 5 shows that EDTA, DTPA, sodium citrate, and sodium oxalate, at the concentrations studied, did not interfere with the ability of magnetite carrier precipitation to remove plutonium from solution. These results may be explained by Fe^{3+}/Fe^{2+} forming insoluble compounds with the salts of these complexing agents and therefore not affecting the precipitation of ^{239}Pu from solution. However, sodium tartrate did interfere significantly. Sodium tartrate was tested with both *in situ*- and *ex situ*-formed magnetite; with *in situ*-formed magnetite, the ^{239}Pu DF values were 6.91 and 1.27, and for *ex situ*-formed magnetite the ^{239}Pu DF was 18.6. If sodium tartrate is present in any of the TRU wastes, an alternative treatment process will need to be implemented.

Filtration

Beaker-scale filtration studies were done to determine the magnetite solids loading on a 5-μm small disc membrane filter (surface area of 17.4 cm^2) and the corresponding pressure drop, at a flow rate of 27.3 mL/min. This flow rate corresponds to the 3.8 L/min rate that will be used in the full-scale ANL treatment system. The tests continued until the filter failed. The maximum pressure drop for bag filters is 60 psi. The magnetite solids loading and the measured pressure drop is illustrated in Fig. 5.

A maximum magnetite solids loading of 12.9 grams was achieved before the filter failed. Since the surface area of the 5-μm bag filters to be used in the full-scale process is approximately 140 times greater than the filters used in the laboratory-scale tests, a solids loading of 1.5 to 2 kg of

Table 5. Effect of Various Complexing Agents on the Final ^{239}Pu Concentration and ^{239}Pu DF.

Complexing Agent	Complexing Agent Conc. (g/L)	Magnetite Conc. (g/L)	Initial ^{239}Pu Conc. (g/L)	Final ^{239}Pu Conc. (g/L)	^{239}Pu DF
EDTA[a]	65	14.8	1.54E-2	1.21E-7	1.27E+5
DTPA[b]	75	14.8	1.54E-2	1.35E-5	1.14E+3
DTPA	75	13.5	1.33E-2	4.44E-5	3.00E+2
DTPA	75	12.9	1.23E-2	5.01E-6	2.46E+3
DTPA	75	14[c]	1.54E-2	1.76E-5	8.75E+2
sodium citrate	147	14.8	1.54E-2	8.00E-7	1.93E+4
sodium oxalate	34	14.8	1.54E-2	2.72E-7	5.66E+4
sodium tartrate	115	14.8	1.54E-2	2.23E-3	6.91E+0
sodium tartrate	115	14.8	1.54E-2	1.21E-2	1.27E+0
sodium tartrate	115	14[c]	1.54E-2	8.27E-4	1.86E+1

[a] EDTA = ethylene diaminetetraacetic acid.

[b] DTPA = diethylenetriaminepentaacetic acid.

[c] Magnetite formed *ex situ*.

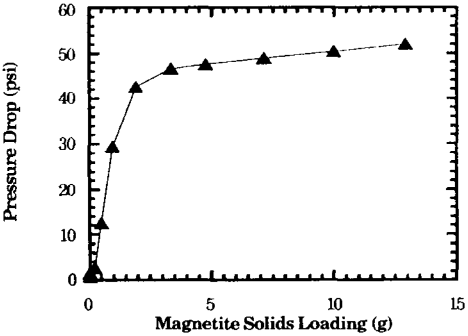

Fig 5. Effect of Magnetite Solids Loading on Pressure Drop

magnetite may be achieved before the bag filters require replacement. (Caution should be taken in correlating the solids loading of the small disc filter and a bag filter.)

CONCLUSIONS

We successfully optimized the carrier precipitation processing parameters, while achieving a concentration of plutonium in the supernatant which is less than 1.51 μg/L (^{239}Pu DF>10^4) and a volume reduction of approximately 75%. The magnetite carrier precipitation is a robust process, and the efficiency is not dependent on processing at elevated temperatures or long mixing times; however, some control of the pH during processing is required. Although the process is sufficiently robust for many cation, anions, and complexing agents, limitations exist for phosphate and tartrate. Cations in the waste solution increase the volume of precipitate that is generated, because of metal hydroxide coprecipitation, and may act to decrease the efficiency of the filtration. Although we have speculated on the structure of the carrier and the mechanisms for this precipitation process, basic studies are essential to verify these hypotheses. Overall, magnetite carrier precipitation is a practical process for treating plutonium waste and is currently planned for implementation by ANL Waste Management Operations.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Waste Management, under Contract W-31-109-Eng-38.

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