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THE USE OF FERROUS NITRATE AS A PLUTONIUM REDUCTANT FOR PARTITIONING PLUTONIUM AND URANIUM IN PUREX PROCESSES

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ABSTRACT

Laboratory-scale studies showed ferrous nitrate–hydrazine solutions to be an attractive alternative to ferrous sulfamate solutions for partitioning plutonium and uranium in a Purex flowsheet. In batch countercurrent tests simulating the processing of fast reactor fuels, more than 99.9% of the plutonium was stripped from the solvent by using as little as 25% of the stoichiometric amount of Fe(II) needed to reduce all of the plutonium. Replacement of the ferrous sulfamate eliminates sulfate (its ultimate decomposition product) from the system, thereby simplifying subsequent processing and waste disposal.

1. INTRODUCTION

Ferrous sulfamate is used in the United States as a plutonium reductant for the partitioning of plutonium and uranium in Purex solvent extraction systems. The iron and sulfate (formed by decomposition of the sulfamate) add significantly to the solids content of the process waste and thereby limit desirable volume reductions. In addition, the sulfate is undesirable because it (1) interferes with plutonium extraction in the second TBP extraction cycle, (2) increases corrosion of the process equipment, and (3) requires addition of calcium to stabilize it in some waste fixation schemes.[1]

The disadvantages of the use of ferrous sulfamate will be of enhanced importance in the treatment of fast reactor fuels because of the large amounts of plutonium present and the correspondingly large amount of reductant required. In one phase of the study of the reprocessing of fast reactor fuels,[2] we are evaluating alternative reductants including uranous nitrate,[3] hydrogen gas,[4] and ferrous nitrate.[2] The first two of these have the advantage of adding no extraneous ions to the system but are more difficult to apply than ferrous nitrate. Although the use of ferrous nitrate would add iron to the waste, it avoids the problems caused by the presence of sulfate. Very promising

results have been obtained with ferrous nitrate solutions (stabilized with hydrazine) in small-scale laboratory experiments. The use of this reductant is the subject of this report.

2. DATA AND DISCUSSION

When ferrous nitrate or uranous nitrate is used for partitioning plutonium and uranium, an auxiliary reductant ("holding reductant" or "stabilizer") must be present. Hydrazine has been used with uranous nitrate.[3] (In the case of ferrous sulfamate, the sulfamate serves this purpose.) The principal function of the holding reductant is to destroy nitrous acid, which is always present to some extent in nitric acid systems. Nitrous acid initiates the oxidation of divalent iron and trivalent plutonium. The reactions have been expressed by Biddle and Miles[5] as follows:

$$M^{n+} + N_2O_4 \rightarrow M^{(n+1)+} + NO_2^- + NO_2 \quad (1)$$

$$H^+ + NO_2^- \rightleftharpoons HNO_2 \quad (2)$$

$$HNO_2 + HNO_3 \rightleftharpoons N_2O_4 + H_2O \quad (3)$$

The reactions are autocatalytic in that 1.5 moles of nitrous acid are produced for each mole consumed. Sufficient holding reductant must be added, therefore, to ensure that all the nitrous acid in the system is destroyed. In the presence of hydrazine, the reaction proceeds in two steps, with formation of hydrazoic acid, HN_3, as an intermediate product:

$$N_2H_4 + HNO_2 \rightarrow HN_3 + 2H_2O \quad (4)$$

$$HN_3 + HNO_2 \rightarrow N_2O + N_2 + H_2O \ . \quad (5)$$

Results of batch plutonium stripping tests that demonstrate the importance of the holding reductant are shown in Table 1. More than 99% of the plutonium was stripped from 15% TBP--n-dodecane (NDD) solvent in 1 min when it was contacted with

Table 1. Effect of Holding Reductant on Efficiency of Plutonium Stripping

Organic phase: 15% TBP--85% NDD containing 4.4 g Pu/liter and 40 g U/liter

Aqueous phase: 0.25 M $Fe(NO_3)_2$--0.2 M HNO_3 solutions plus a holding reductant

Contact: Batch at organic/aqueous phase ratio of 7/1

Holding Reductant	Plutonium Stripped, %		
	1 min	5 min	30 min
None	73.7	71.5	71.3
0.025 M sulfamic acid	99.2	99.2	99.0
0.10 M hydroxylamine nitrate	99.2	99.4	99.4
0.025 M hydroxylamine nitrate	99.0	99.1	99.2
0.20 M hydrazine	99.1	99.1	99.3
0.025 M hydrazine	99.3	99.4	-
0.05 M hydroquinone	99.4	99.4	-

one-seventh volume of 0.25 M $Fe(NO_3)_2$--0.2 M HNO_3 solution containing hydrazine, hydroxylamine nitrate, sulfamic acid, or hydroquinone. Increasing the contact time to 30 min did not appreciably affect the results. With no holding reductant present, only about 70% of the plutonium was stripped. The amount of iron used in these tests was about 2 moles per mole of plutonium. Results with a hydrazine concentration of 0.025 M were as good as those obtained when the concentration was 0.20 M. These data, however, do not provide an indication of the amount of holding reductant that would be needed in an actual process, where the amount of nitrous acid present is expected to be much higher than the extremely low amounts that probably were present in these tests and in the tests described in the subsequent sections.

Distribution data indicate that most of the nitrous acid in the TBP--HNO_3--$UO_2(NO_3)_2$ system[5] will be extracted into the solvent and carried into the partitioning system. Nitrous acid is formed by the fuel dissolution reactions and, consequently, is present in the aqueous feed from the dissolver. In addition, sodium nitrite is usually added to adjust the valence of the plutonium to Pu(IV) prior to extraction. The nitrous acid in the feed is usually the principal source of the nitrous acid found in the extraction system. The concentration of nitrous acid in the feed can be decreased to a relatively low value by heating and/or sparging the solution in the feed adjustment step. For example, in a laboratory test, heating a simulated aqueous feed for 1 hr at 40-50°C reduced the nitrous acid concentration from 0.09 N to less than 0.004 N. In addition to the nitrous acid entering in the aqueous feed, small amounts can be formed in the solvent extraction system by radiolytic degradation of nitric acid.

It is obvious from the above discussion that the amount of hydrazine needed for effective partitioning is principally dependent on the amount of nitrous acid present and thus can vary appreciably. Therefore, hydrazine requirements cannot be established except in an actual operating radiochemical facility. It appears, however, that the required hydrazine concentration in the strip solution, assuming an organic/aqueous feed ratio of 6 to 1, should not be higher than 0.2 M and probably

would be considerably lower.

2.1 Ferrous Iron Requirements

In batch stripping tests with ferrous nitrate--hydrazine solutions, 97.7% of the plutonium was stripped in a single contact at an organic/aqueous phase ratio of 7/1 when the stoichiometric amount of Fe(II) required to reduce the plutonium was used (Table 2). With 100% excess iron, about 99% of the plutonium was stripped. However, if the acid concentration in the feed strip solution is kept low, efficient partitioning of plutonium and uranium can be accomplished in a countercurrent system by using much smaller amounts of iron (i.e., with reduction of only part of the plutonium). For example, in a batch countercurrent test, good results were obtained by using only about 25% of the amount of iron needed to reduce all of the plutonium (see Sect. 2.2.1).

2.2 Batch Countercurrent Tests

Excellent results were obtained in batch countercurrent tests that demonstrated the use of ferrous nitrate--hydrazine reductant. In a test using four stripping and five scrub (uranium reextraction) stages, the stripping of plutonium was greater than 99.98% complete (Table 3). The Pu/U and U/Pu decontamination factors were 5×10^5 and 1×10^4, respectively. About 100% excess iron was used in this test. Each contact of the phases was for 1 min.

2.2.1 Partitioning with Less Than the Stoichiometric Amount of Ferrous Nitrate

The U/Pu(IV) separation factor in the TBP--dilute nitric acid system is about 5. Thus effective separation of the plutonium and uranium can be obtained with dilute nitric acid alone when a relatively large number of stages are used and very careful process control is maintained. However, the use of dilute acid containing a small amount of reductant (considerably less than that needed to reduce all of the plutonium) appears to be attractive. Under these conditions most of the plutonium is stripped as Pu(IV). The reductant improves the separation efficiency, particularly in the

Table 2. Reductive Stripping of Plutonium with Ferrous Nitrate--Hydrazine

Organic phase: 15% TBP--85% NDD containing 2.2 g Pu/liter and 40 g U/liter

Aqueous phase: $Fe(NO_3)_2$--0.2 M HNO_3--0.013 M N_2H_4

Contact: Batch at organic/aqueous phase ratio of 7/1

$Fe(NO_3)_2$ Conc. (M)	Approximate Excess Fe(II)[a] (%)	Pu Stripped in	
		1 min	5 min
0.065	0	97.7	97.7
0.071	10	97.2	96.1
0.077	20	97.3	95.0
0.084	30	98.8	97.6
0.097	50	98.8	97.6
0.129	100	99.1	98.9

[a]Excess over stoichiometric requirement of 1 mole of Fe(II) per mole of Pu.

Table 3. Batch Countercurrent Partitioning of Plutonium and Uranium with Ferrous Nitrate--Hydrazine

Organic feed: 15% TBP--85% NDD containing 3.7 g Pu/liter and 35 g U/liter

Strip solution: 0.2 M HNO_3--0.20 M $Fe(NO_3)_2$--0.013 M N_2H_4

Organic scrub: 15% TBP--85% NDD

Flow ratios, feed/strip/scrub: 7/1/2

	Conc. in Organic Phase (g/liter)		Conc. in Aqueous Phase (g/liter)	
Stage	Pu	U	Pu	U
Strip-4	0.00025	27.2	0.0074	46.5
-3	0.00031	32.6	0.094	55.9
-2	0.0017	33.4	2.73	45.6
-1	0.029	33.0	27.2	19.3
Organic Feed	3.7	34.7	-	-
Scrub-1	0.29	10.2	27.9	2.3
-2	0.30	0.81	24.8	0.062
-3	0.55	0.064	27.5	0.010
-4	0.57	0.012	27.7	0.001
-5	0.50	0.006	27.4	<0.001

plutonium-dilute end of the system, and helps ensure complete recovery* of plutonium from the solvent.

In a batch countercurrent test, more than 99.9% of the plutonium was stripped from 15% TBP--NDD with 0.15 M HNO_3--0.01 M N_2H_4 solution containing about 25% of the amount of Fe(II) that would have been needed to reduce all of the plutonium (Table 4). The plutonium product solution contained 17.7 g of plutonium and 14.4 g of uranium per liter. The uranium content of this solution (about 8% of the total uranium) could, of course, have been decreased to a much lower level by adding more scrub stages; only three were used in this test. In processing fast reactor fuels, a highly effective separation of the uranium from the plutonium product should not be necessary since additional uranium will be removed in the final plutonium purification (ion exchange or amine extraction) cycle. Also, the presence of small concentrations of uranium should not interfere with the preparation of the plutonium oxide fuel (e.g., by the sol-gel process) for recycle to the reactor.[6]

The acid concentration of the strip solution in the test just described was only 0.15 M. However, the acid concentration in the aqueous phase in stages where the plutonium concentration was relatively high (feed stage and scrub system) was about 1 M since nitric acid was scrubbed from the organic feed. These conditions with respect to acid and Pu(IV) concentrations are far from the region in which plutonium polymer forms.[7]

2.3 Preparation of Ferrous Nitrate Solutions

Ferrous nitrate solutions are easily prepared and are relatively stable. In our studies, ferrous nitrate solutions up to 0.8 M in concentration were prepared by the reaction of iron metal (filings) with acid solutions of ferric nitrate. The Fe(II)

*The presence of some reductant is particularly important if the solvent contains significant concentrations of TBP degradation products (mono- and dibutylphosphoric acids) that retain plutonium.

Table 4. Batch Countercurrent Partitioning of Plutonium and Uranium, with Reduction of Only Part of the Plutonium

Organic feed: 15% TBP--NDD containing 2.94 g Pu/liter and 31.4 g U/liter

Strip solution: 0.15 M HNO_3--0.02 M $Fe(NO_3)_2$--0.01 M N_2H_4

Flow ratios, feed/strip/scrub: 6/1/1

	Conc. in Organic Phase (g/liter)		Conc. in Aqueous Phase (g/liter)	
Stage	Pu	U	Pu	U
Strip-4	0.0012	24.2	0.55	47.0
-3	0.079	31.2	6.6	62.6
-2	1.05	33.1	18.9	63.0
-1	2.23	32.5	19.2	52.5
Organic Feed	2.94	31.4	-	-
Scrub-1	2.52	32.4	20.5	44.0
-2	3.00	26.0	20.0	28.9
-3	3.44	17.0	17.7	14.4

is formed principally by the reaction of iron metal with ferric nitrate:

$$Fe^{o} + 2Fe(NO_3)_3 \rightarrow 3Fe(NO_3)_2 \ , \qquad (6)$$

but is also formed by the reaction of iron metal with dilute nitric acid:

$$4Fe^{o} + 10HNO_3 \rightarrow 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O \ . \qquad (7)$$

Specifically, a 0.15 M HNO_3--1 M $Fe(NO_3)_3$ solution was allowed to react with an excess of iron filings for about 2 hr. The mixture was then filtered and reacidified to give a final HNO_3 concentration of about 0.1 M. Analyses showed less than 4% of the iron in solution was Fe(III).

In process application, a ferrous nitrate solution could be prepared on a continuous basis simply by percolating an acid solution of ferric nitrate, containing a small amount of hydrazine, through a column of iron filings.

Remy[8] states that "Fe(II) has but small tendency to become oxidized to the +3 state in dilute acid at ordinary temperatures" and that "the stability of Fe(II) salts in solution can be raised to a considerable extent by adding an excess of acid to repress hydrolysis." We found that a concentrated $Fe(NO_3)_2$ solution (stored in a stoppered bottle at ambient temperature) oxidized slowly; for example, the Fe(II) concentration of a typical solution decreased from 0.78 N to 0.70 N after setting for 5 days. The addition of small amounts of hydrazine to the solution increased the stability of the solution by destroying nitrite (which catalyzes the oxidation).

2.4 Safety Aspects in the Use of Hydrazine

The major potential hazard in using hydrazine in an aqueous solution in the TBP-HNO_3-$UO_2(NO_3)_2$ system would be the formation of hydrazoic acid as an intermediate product by the reaction of nitrous acid with hydrazine [Eqs. (4) and (5), p. 2]. Hydrazoic acid could form in the partitioning step and also during a subsequent feed adjustment step when compounds such as $NaNO_2$ or nitrogen oxides are used to oxidize Pu(III) to Pu(IV) in preparation for the next purification cycle.

Scientists at the Savannah River Laboratory have made a study of the hazards of hydrazoic acid in connection with the use of hydrazine as a holding reductant and uranous nitrate as the partitioning reagent.[3e] In this study they showed that hydrazoic acid never reaches the critical explosive concentration (4.7 M in aqueous solution) in their process since dilute solutions (< 0.2 M) of hydrazine are used. By analogy, there should be no hazard in using ferrous nitrate—hydrazine solutions as proposed in this report since the maximum hydrazine concentration should be 0.2 M. However, the extraction of hydrazoic acid into the organic phase may result in the formation of sodium azide in the alkaline solvent wash solutions. Thus, the hydrazoic acid should be destroyed by treatment with sodium nitrite[3e] before being discharged into waste tanks.

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