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GAS FORMATION IN ANION EXCHANGE RESIN BEDS

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GAS FORMATION IN ANION EXCHANGE RESIN BEDS

by

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ABSTRACT

Gas formed in fixed beds of anion exchange resin is difficult to remove and causes channeling and reduction in flows. The major source of gas in resin beds used to recover actinides from nitrate solutions is the reaction of sulfamate ion with nitrous acid, which produces nitrogen. Two approaches to minimizing gas formation are: completely destroy sulfamate in a feed pretreatment, or replace sulfamate with a non-gas-forming stabilizer.

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GAS FORMATION IN ANION EXCHANGE RESIN BEDS

INTRODUCTION

Plutonium and neptunium are recovered from aqueous nitrate solutions by anion exchange processes.(1) In a typical anion exchange cycle, neptunium is:

- Adjusted to the strongly absorbed Np(IV) state in strong nitrate solution by adding stabilized ferrous ion.
- Absorbed on a bed of anion exchange resin.
- Washed free of fission products or other contaminants.
- Eluted with dilute nitric acid.

A widely used procedure for the valence adjustment when both neptunium and plutonium are to be absorbed involves the addition of ferrous sulfamate to the feed solution; hydrazine nitrate is also often added as an additional stabilizer. Ferrous ion rapidly reduces plutonium to Pu(III) and neptunium to Np(IV). The adjusted solution is then heated moderately to oxidize the excess ferrous ion and to oxidize Pu(III) to Pu(IV). In strong nitrate solution, Pu(IV) and Np(IV) are not appreciably oxidized by the heat treatment.

One disadvantage of this type of process cycle is that gas forms when the treated feed solution is passed through an anion exchange bed. The gas that accumulates in the bed is difficult to remove and causes channeling and reduction in flows. Gas accumulation is particularly troublesome with unrestrained beds of resin, which are used in some processes.(2)

In the work described in this report, the composition of the gas formed from feeds treated with ferrous sulfamate and the mechanism of gas formation were first investigated. Methods for reducing or eliminating gas formation were then tested.

SUMMARY

The gas formed in anion exchange beds used to recover neptunium or plutonium from nitrate solutions is predominantly nitrogen when ferrous sulfamate is used as a valence adjusting reagent. This nitrogen results from the reaction of residual sulfamate ion with traces of nitrous acid.

Gas in the anion exchange column was avoided by a feed pretreatment step in which all of the sulfamate ion was destroyed by reaction with an excess of nitrous acid. Vigorous outgassing of the treated feed was necessary prior to passing the solution through the column. The treatment did not result in significantly higher oxidative losses of neptunium or plutonium in laboratory tests under normal conditions, but in plant runs of long duration with high concentrations of ^{238}Pu, higher losses were observed. These higher losses were attributed to radiolytic oxidation by ^{238}Pu alpha activity.

Preliminary attempts were made to prepare ferrous nitrate for use as a valence adjusting reagent with a stabilizer that would have less tendency than sulfamate ion to form gas. The most satisfactory reagent was a solution of ferrous nitrate stabilized against oxidation by aminoguanidine and hydrazine. Preliminary tests showed that process solutions treated with this reagent formed less gas in anion exchange columns; however, a thorough evaluation of this method of treatment was not completed.

DISCUSSION

MECHANISM OF GAS FORMATION

Laboratory tests indicated that nitrogen is the major gas formed in the feed solution, and that it is formed by the reaction of sulfamate ion with nitrous acid. The nitrous acid arises from the reduction of nitric acid by ferrous ion and from radiolytic decomposition of nitric acid.

In a typical valence adjustment with ferrous sulfamate and without hydrazine, the solution is adjusted to 0.05M ferrous sulfamate. After a short interval to allow reduction of the actinides, the solution is heated to 55°C for 30 minutes. Only a small fraction of the ferrous ion is normally required to reduce the actinides; therefore, the heat treatment oxidizes the major portion of the remaining ferrous ion:(3,4)

$$2Fe^{2+} + HNO_3 + 2H^+ \rightarrow 2Fe^{3+} + HNO_2 + H_2O \qquad (1)$$

When one liter of 0.05M Fe^{2+} is oxidized, 0.025 mol of HNO_2 is produced, 0.025 mol of sulfamic acid is consumed, and 560 cc (STP) of nitrogen gas are produced:

$$HOSO_2NH_2 + HNO_2 \rightarrow H_2SO_4 + N_2 + H_2O \qquad (2)$$

Approximately the predicted quantity of gas was released during the heating of synthetic process solutions with efficient agitation. Mass spectrometric analysis confirmed that the gas was mostly nitrogen. With inefficient agitation and outgassing, large quantities of the gas were retained in solution and released later when the solution was passed through an ion exchange bed. Analysis of residual sulfamate after heat treatment gave an average concentration of about 0.08M, which agrees with the simple proposed mechanism (the initial sulfamate concentration was 0.1M). This residual sulfamate in the feed to an anion exchange bed can react with nitrite formed in the column to release additional nitrogen gas.

In processing actinides, the main source of nitrite formation in the beds is probably alpha radiolysis of nitrate ion. For example, columns containing resin loaded with highly active ^{238}Pu show considerably more gassing than columns containing ^{239}Pu or ^{237}Np.

In valence adjustments in which a combination of ferrous sulfamate and hydrazine are used in the feed, and the solution is heated, Reaction 1 is unaltered, but the nitrous acid formed may react with either sulfamic acid or hydrazine by Reaction 2 or 3:(5)

$$N_2H_5^+ + HNO_2 \rightarrow HN_3 + H^+ + 2H_2O \qquad (3)$$

$$HN_3 + HNO_2 \rightarrow N_2 + N_2O + H_2O \qquad (4)$$

The end result is the formation of nitrogen and oxides of nitrogen, but the quantity of gas may be reduced by formation of the intermediate (hydrazoic acid) without subsequent formation of nitrogen.

These mechanisms suggest two approaches for reducing or eliminating the problem. One approach retains the use of ferrous sulfamate and hydrazine, but replaces the customary heat treatment with a chemical treatment in which the gas-forming reagents, sulfamic acid and hydrazine, are destroyed completely before the anion exchange step. The other approach retains ferrous ion as the primary reductant, but substitutes a non-gas-forming stabilizer in place of sulfamate ion. Both approaches were tested and are described in the following sections.

CHEMICAL PRETREATMENT OF PROCESS SOLUTIONS

A simple chemical treatment for the destruction of sulfamic acid and hydrazine is the addition of excess sodium nitrite. In this method, the valence of neptunium or plutonium is first adjusted by the addition of ferrous sulfamate, and the excess ferrous, sulfamate, and hydrazine are then destroyed by the addition of sodium nitrite. Finally, excess nitrite is removed from the solution by air sparging. Two major considerations in testing this method were the ability to prevent re-oxidation of Pu(IV) and Np(IV) during and after the nitrite treatment, and the ability to outgas the solution thoroughly prior to passing it through the ion exchange column.

Tests showed that the stoichiometric amount of nitrite plus a 25% excess was required for complete destruction of sulfamate and hydrazine in process solutions containing 6 to 8M HNO_3 when 5M sodium nitrite was added at a rapid rate with vigorous agitation of the solution. Vigorous air sparging of the treated solution was necessary for thorough outgassing to avoid subsequent gas release in the column.

In solutions of low acidity and high salt content, the outgassing was particularly difficult, suggesting the possible formation of a metastable intermediate in the reaction between sulfamate ion and nitrous acid. This possibility was explored, and the conditions under which an intermediate is formed are described elsewhere.(e)

Laboratory tests with simulated process solutions containing ^{237}Np and ^{238}Pu demonstrated that the chemical treatment followed by vigorous air sparging eliminated gas formation in the columns without adversely affecting product losses. The oxidation of Pu(IV) and Np(IV) to higher, weakly absorbed valence states is slow in strong nitrate solution because of the strong complexing of the tetravalent ions by nitrate. Results of a typical comparative test are shown in Table I. In the column test of the nitrite treatment, no gas was observed in the column and faster flows were attainable. The slight increase in plutonium loss may be attributed to the higher concentration of sulfate ion produced in the feed by Reaction 2.

TABLE I

Column Test of Chemical Treatment

Resin: "Dowex"* 1-X4 resin, 30-50 mesh, 20 ml

Bed Dimensions: 0.61 cm^2 x 33 cm

Feed Volume: 200 ml

Feed Concentration: 6.0M HNO_3, 0.5M $Al(NO_3)_3$, 0.35 g ^{238}Pu/l, 1.45 g ^{237}Np/l

Feed Treatment	Losses to Effluent, %	
	^{238}Pu	^{237}Np
Heat Treatment:		
1. Adjust to 0.05M $Fe(NH_2SO_3)_2$. 2. Heat at 55°C for 30 minutes.	0.21	1.2
Nitrite Treatment:		
1. Adjust to 0.05M $Fe(NH_2SO_3)_2$. 2. Add 0.125M $NaNO_2$. 3. Air Sparge.	0.33	1.1

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* "Dowex" is a trademark of Dow Chemical Co.

The nitrite treatment was tested at plant scale with a 25-liter bed of resin. Flows were increased by 50%, indicating that gas formation was diminished, but effluent losses of ^{237}Np and ^{238}Pu were 2- to 5-fold higher than in laboratory tests. This extra loss was attributed to slow oxidation by radiolysis over the 4-fold longer periods of time required for the plant runs. Additional work would be necessary to define satisfactory conditions to achieve low losses when highly radioactive isotopes such as ^{238}Pu are processed. The method can be more readily applied to processes involving ^{239}Pu or ^{237}Np.

ALTERNATIVE STABILIZERS

Tests were made to find an effective stabilizer that would produce less gas. Ferrous nitrate was prepared by the controlled dissolution of iron powder in nitric acid containing a stabilizer. A known amount of iron powder was added in small increments over 4 to 6 hours to 1 to 2M HNO_3 containing 0.2 to 0.4M stabilizer. The temperature was maintained below 30°C. The acidity was kept above 0.1M by adding 5M HNO_3. The acid addition was carefully controlled toward the end so that the final solution was about pH 0.8. The final solution contained about 1.5M ferrous nitrate and about 0.2M stabilizer.

The stability of ferrous nitrate prepared in the presence of the following stabilizers was tested:

ascorbic acid
amidoguanidine
guanidine
urea
guanylurea
semicarbazide
isoascorbic acid
aminoguanidine
formamide
thiourea
sulfamic acid
hydrazine

Of these, the most promising were aminoguanidine and hydrazine. Less than 1% of the ferrous ion in a solution containing 1.53M $Fe(NO_3)_2$, 0.23M aminoguanidine, and 0.4M HNO_3 was oxidized after one month at 25°C. Similar results were found for hydrazine-stabilized ferrous nitrate. Some solutions that were stable for several months are listed in Table II.

TABLE II

Stabilized Ferrous Nitrate Solutions

Solution	pH
1.66M ferrous nitrate-0.68M hydrazine nitrate	0.5
1.08M ferrous nitrate-0.37M hydrazine nitrate	0.8
1.03M ferrous nitrate-0.25M aminoguanidine carbonate	0.6
1.32M ferrous nitrate-0.25M aminoguanidine sulfate	0.8

The use of hydrazine in the preparation of ferrous nitrate produces hydrazoic acid, which can be hazardous under certain conditions.(4) To minimize the concentration of hydrazoic acid, ferrous nitrate was prepared in the presence of aminoguanidine; then hydrazine was added to impart added stability. Solutions prepared by this method were stable for several months. Hydrazoic acid was not detected in the solutions until three weeks after preparation.

Spectrophotometric studies showed that ferrous nitrate stabilized with aminoguanidine and hydrazine was satisfactory for controlling the valences of plutonium and neptunium. In column tests, less gas was formed with feed treated with this reagent than in comparative runs treated with ferrous sulfamate and heat. The work was terminated, however, before a thorough evaluation could be made. Additional work that would be required before the reagent could be applied for general process use would include:

- A hazards evaluation of hydrazoic acid and possible intermediates formed by aminoguanidine.
- Tests in the presence of high levels of radioactivity.
- Large-scale column tests.

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