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THE DECONTAMINATION OF DISSOLVED U-AL FUEL BY SIMULTANEOUS TREATMENT WITH GELATIN AND MnO_2

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THE DECONTAMINATION OF DISSOLVED U-AL FUEL BY SIMULTANEOUS TREATMENT WITH GELATIN AND MnO_2

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ABSTRACT

The method of decontaminating enriched U-Al fuel solutions from fission products by simultaneous treatment with gelatin and MnO_2 was investigated to determine the effects of $Al(NO_3)_3$ and HNO_3 concentrations and to optimize operating conditions. Heating at 70 to 80°C after $KMnO_4$ addition for differing periods of time had no significant effect on cake volume or the decontamination factor (DF). Cake volume and DF both decreased markedly with increased HNO_3 and $Al(NO_3)_3$ concentrations. The decreased particle size associated with the small cake volumes at high $Al(NO_3)_3$ concentrations is a potential cause of problems in filtration and centrifugation of the cake. To achieve adequate decontamination and efficient cake removal, HNO_3 and $Al(NO_3)_3$ should be adjusted to <1M before the gelatin-MnO_2 treatment and concentration of the feed for solvent extraction should be performed after the strike. Retention of uranium, neptunium, and plutonium in the MnO_2-gelatin cake is decreased to acceptable levels by five washes with 0.1M HNO_3.

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THE DECONTAMINATION OF DISSOLVED U-Al FUEL BY SIMULTANEOUS TREATMENT WITH GELATIN AND MnO_2

INTRODUCTION

MnO_2 precipitation[1-7] and gelatin treatment[8] have been used as head-end operations to remove fission products and to clarify solutions of nuclear fuels prior to solvent extraction processing. The combined strike, simultaneous formation of MnO_2 and gelatin precipitates, has been employed at the Savannah River Plant (SRP) as a head-end treatment in processing enriched U-Al and U_3O_8-Al fuels.

In miniature mixer-settler tests of a new (7½% TBP) enriched uranium flowsheet with actual SRP feed solutions, the combined strike produced a precipitate that settled quite slowly and filtered inefficiently. Plant operation with the same feed had shown nearly quantitative carryover of manganese into the feed, indicating that the MnO_2 cake either redissolved or centrifuged poorly. This study was therefore conducted to determine which process variables were responsible for the inefficient operation of the combined strike. The effects of simmer time, aluminum nitrate, and nitric acid concentration on cake volume and decontamination efficiency were investigated. In addition, retention of U, Np, and Pu in the MnO_2-gelatin cake was studied as a function of aluminum nitrate and nitric acid concentrations.

Previous studies include an investigation of MnO_2 precipitation (without gelatin) in nitric acid solutions containing aluminum nitrate.[5] Also, several tests have been conducted at SRP to determine the effect of various operating conditions on Zr-Nb decontamination by MnO_2 precipitation and by the combined strike.

EXPERIMENTAL

Combined MnO_2-gelatin strikes were conducted by adding 1.4 ml of 1% gelatin and 1.8 ml of 25% $Mn(NO_3)_2$ to 200 ml of the desired HNO_3-$Al(NO_3)_3$-$UO_2(NO_3)_2$ solution, heating the mixture to 70 to 80°C with stirring at 800 rpm, and adding 10.6 ml of 3% $KMnO_4$ at a rate of 2 ml/min. The resulting slurry was maintained at 70 to 80°C ("simmered") with stirring, usually for 15 min. Four samples (10 to 15 ml) of each slurry were centrifuged 10 min at 1700 rpm, and the four cake volumes were measured and averaged. Cakes were washed five times with ∿2 cake volumes of 0.1M HNO_3 and dissolved in HNO_3-$NaNO_2$ for uranium and gross α(Np-Pu) analyses.

For measurement of decontamination factors, HNO_3-$Al(NO_3)_3$-$UO_2(NO_3)_2$ solutions were prepared containing 10^{-4}M each of cesium, ruthenium, zirconium, and cerium; these solutions were then spiked with diluted SRP feed solution containing $\sim 10^9$ gamma dis/(min-ml) of mixed fission products. Decontamination factors were obtained from gamma pulse-height, crystal scintillation, and Geiger-Mueller counting (for beta emitters) of samples before and after precipitation. Corrections were made for volume changes due to reagent additions, but volume changes due to evaporation were neglected unless prolonged simmer times were used.

Gelatin, 50% $Mn(NO_3)_2$, and 6% $KMnO_4$ were obtained from SRP. All other chemicals were reagent grade.

RESULTS

Effect of Simmer Time

The effect of varying the simmer time following $KMnO_4$ addition was investigated; a time of 1 to 2 hr at 70 to 80°C is normally used in plant operations.[7] As shown in Figure 1, simmer time had no significant effect on the cake volume,* and no effect on filtering or centrifuging efficiency would be expected. Also, the data in Table 1 indicate that decontamination factors (DFs) are not strongly affected by the length of the simmering period. In actual feed solutions containing high levels of activity, DFs have been observed to decrease with prolonged simmer times.[2] Therefore, an extended simmer time is unnecessary and possibly deleterious. A simmer time of 15 min was used in this study. The choice of other operating conditions, such as temperature and stirring speed, was based on previous studies[5-7] and/or experimental equipment limitations.

Effect Of $Al(NO_3)_3$ And HNO_3 Concentrations On Cake Volume

Increased $Al(NO_3)_3$ and HNO_3 concentrations resulted in decreased MnO_2-gelatin cake volumes (Figure 2). In a previous investigation of MnO_2 precipitation without gelatin, cake volumes also decreased as HNO_3 increased, but, in contrast to the results of the present study, cake volumes were observed to increase as $Al(NO_3)_3$ increased.[5] This difference cannot be attributed to the presence of gelatin because our results for 2M HNO_3 were essentially unchanged when gelatin was omitted.

*Cake volume is a useful criterion for judging performance of the precipitation because it is related to the density, structure, and surface area of the MnO_2.

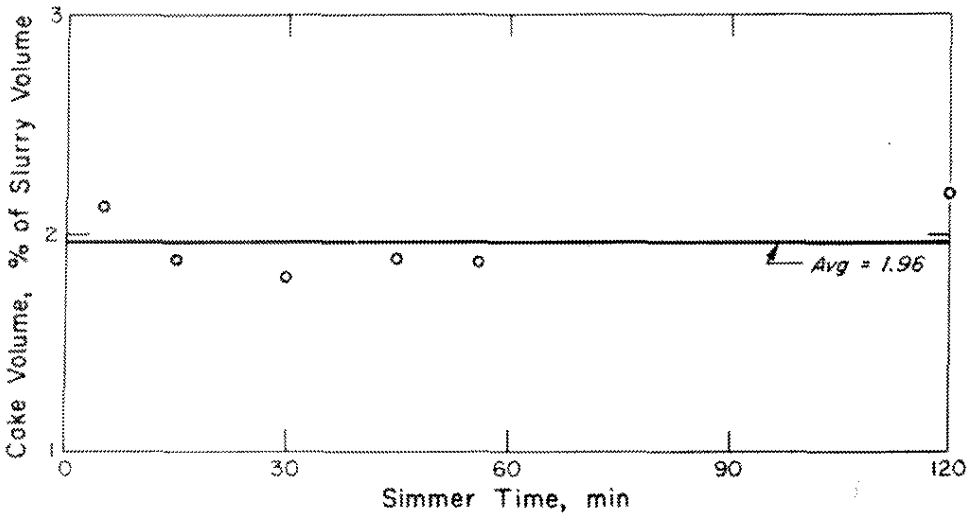

FIGURE 1. Effect of Simmer Time on MnO_2-Gelatin Cake Volume [Precipitated from 1.0M HNO_3-2.5M $Al(NO_3)_3$]

TABLE 1

Effect of Simmer Time on Decontamination[a]

Simmer Time, min	*Decontamination Factor*				
	Ru	*Cs*	*Ce*	*Zr*	*Nb*
5	1.3	1.0	1.0	4.6	3.7
15	1.7	1.0	1.0	4.3	3.6
30	1.4	1.0	1.1	3.6	3.4
120	1.5	1.2	1.3	3.7	3.9

a. Solution composition was 1M HNO_3-2M $Al(NO_3)_3$-4 g U/ℓ.

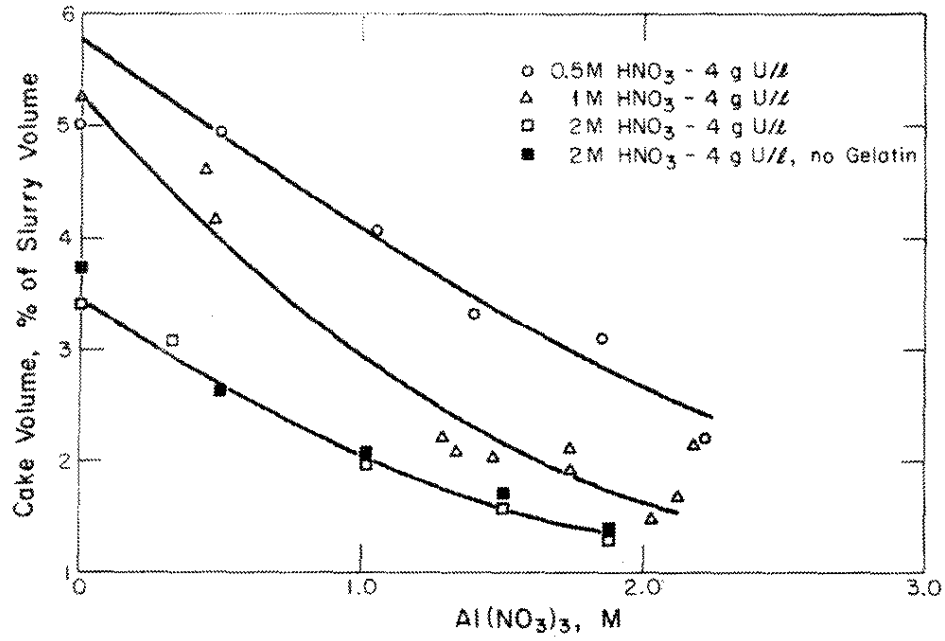

FIGURE 2. Effect of Aluminum Nitrate and Nitric Acid Concentrations on MnO_2-Gelatin Cake Volume

A decrease in cake volume offers some advantages. For example, in cake washing, small cake volumes increase the degree of dilution caused by each fresh wash solution.[6] In addition, precipitates with small volumes have been centrifuged more easily in Purex processing. However, the latter effect does not apply to the type of solutions used in this study; precipitates with small cake volumes settled very slowly in the viscous, concentrated $Al(NO_3)_3$ solutions, and the solutions were often cloudy after centrifugation. The small particles produced at aluminum concentrations >1M often passed through medium frit filters in laboratory tests. In plant operations, small particle size could result in increased carryover of MnO_2 into the centrifuge run tank and possible reaction during storage with radiolytically produced nitrite. Subsequent valence adjustment could be less efficient due to the reaction of entrained MnO_2 with the reductant. Both occurrences are possible explanations for the recently observed high manganese concentration in SRP solvent extraction feed.

Effect of $Al(NO_3)_3$ and HNO_3 Concentrations on Decontamination

The effect of HNO_3 concentration on decontamination efficiency is shown in Figures 3 and 4. Decontamination factors for zirconium and niobium are very sensitive to HNO_3 concentration, but DFs for the other fission products are almost unchanged by

varying the HNO_3 concentration from 0.5 to 2M. Similar effects were observed when the $Al(NO_3)_3$ concentration was increased in 1M HNO_3 (Figure 5). In this case, the DF for ruthenium also decreased markedly, although somewhat irregularly, as $Al(NO_3)_3$ increased. The results of this work are in agreement with those of previous plant tests on decontamination of enriched uranium solutions with the combined strike (Table 2). The plant test data indicate that a Zr-Nb DF of >10 can be attained with a combined strike in a sufficiently dilute raw metal solution. Increasing the HNO_3 and $Al(NO_3)_3$ concentrations by evaporation before the strike severely decreased the attainable DF.

Henry[5] previously investigated the effect of $Al(NO_3)_3$ concentration on DFs obtained in 0.5M HNO_3 by MnO_2 precipitation without gelatin. DFs reported for 0.5M HNO_3 in the present report are comparable to those of the previous work for zirconium, niobium, and ruthenium, but the gross gamma and gross beta DFs are lower. The lower results may be caused by the use of different fission product mixtures in the experiments rather than from an effect of the presence of gelatin.

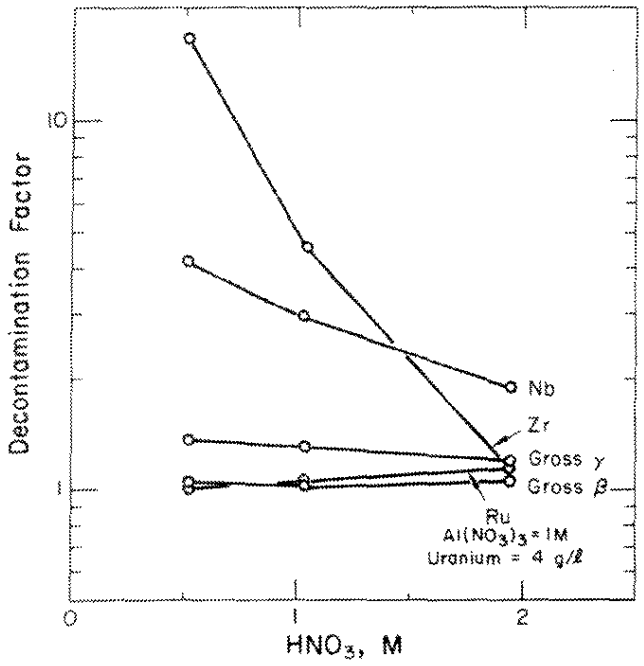

FIGURE 3. Effect of Nitric Acid Concentration on Decontamination Factors in 1M $Al(NO_3)_3$ Solutions

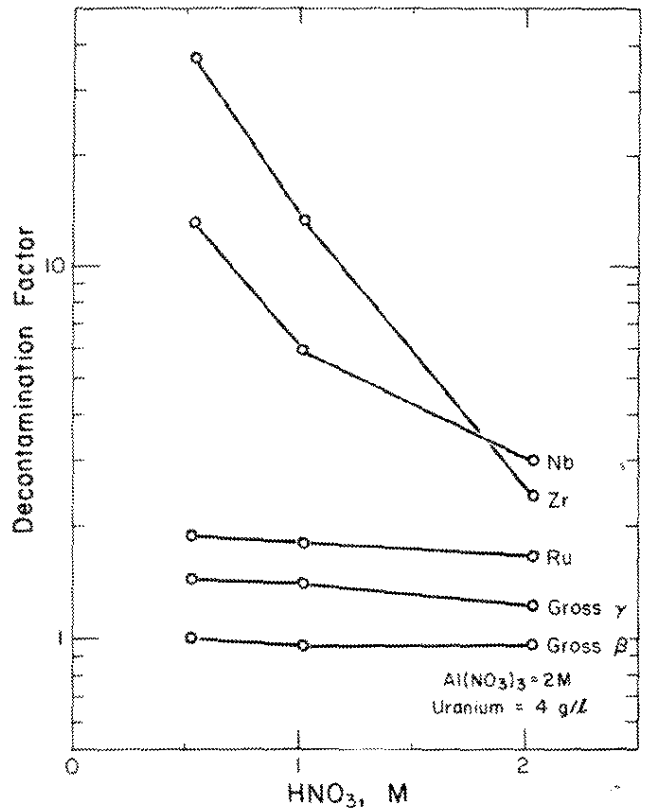

FIGURE 4. Effect of Nitric Acid Concentration on Decontamination Factors in 2M $Al(NO_3)_3$ Solutions

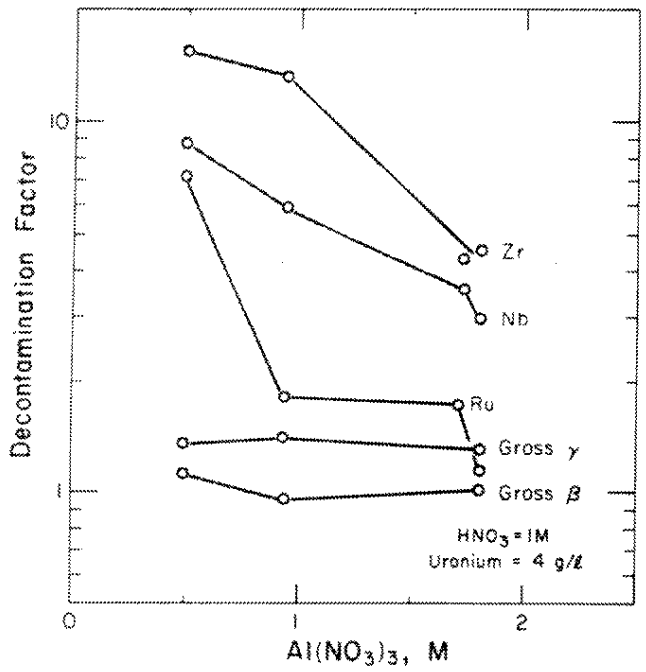

FIGURE 5. Effect of Aluminum Nitrate Concentration on Decontamination Factors in 1M HNO_3 Solutions

TABLE 2

Plant Tests of Combined MnO_2-Gelatin Strike

Test Solution	*HNO_3, M*	*$Al(NO_3)_3$, M*	*Zr-Nb DF*
a	2.3	1.6	1.9
b	0.6	0.4	12
b	0.6	0.4	14
c	1.4	0.8	27
c	1.4	0.8	14

a. Concentrated dissolver solution

b. Diluted dissolver solution

c. Raw metal solution as received from dissolver

Retention of Uranium, Neptunium, and Plutonium in the MnO_2-Gelatin Cake

Retention of uranium and neptunium-plutonium in the unwashed MnO_2-gelatin cake varied from 2 to 4.5% and 2.4 to 5.1% respectively. In agreement with a previous study,[5] uranium retention decreased as the HNO_3 concentration increased. No definite relationship could be established between product retention and $Al(NO_3)_3$ concentration. As shown in Figure 6, four to five washes with 0.1M HNO_3 were sufficient to remove nearly all of the adsorbed uranium. This procedure decreased uranium retention to <0.15% and neptunium-plutonium retention to <0.2% for all solutions tested. Similar losses have been reported in MnO_2 precipitations with no gelatin present.[5]

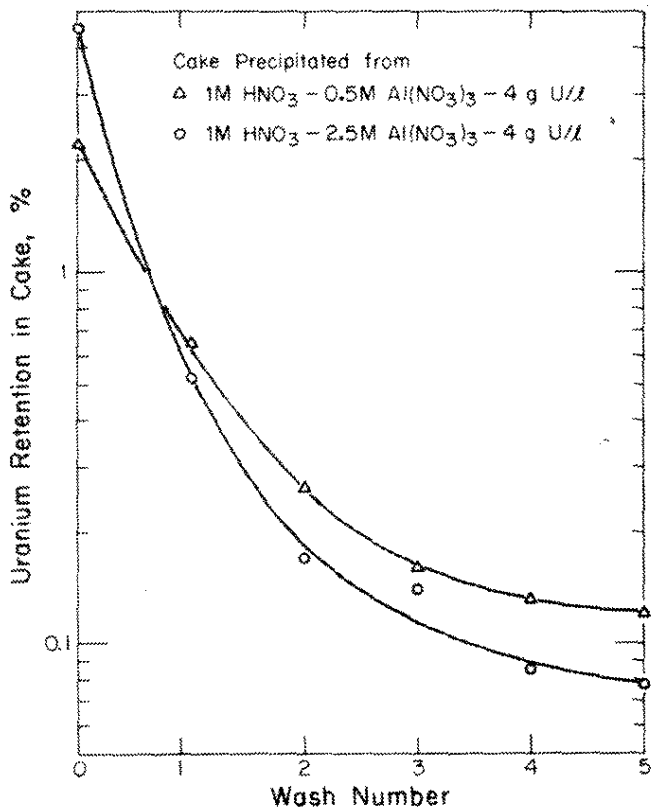

FIGURE 6. Washing of Centrifuged MnO_2-Gelatin Cake

CONCLUSIONS

Based on previous studies and the results of this work, the optimum conditions for conducting the combined MnO_2-gelatin strike at SRP are:

HNO_3:	<1M
$Al(NO_3)_3$:	<1M
Temperature:	70 to 80°C
Stirring Speed:	Maximum rate commensurate with safe operation
Simmer Time:	Minimum permitted by operating requirements
Cake Washes:	5 washes with 0.1M HNO_3

Current plant operation includes concentrating the dissolver solution to ∿1.8M Al^{3+} before conducting the combined strike. Then, after slight dilution by jet transfers, the feed solution is adjusted for solvent extraction processing. To achieve the optimum HNO_3 and $Al(NO_3)_3$ concentrations, either the strike must be performed before concentration of the dissolver solution, or the solution must be diluted before the strike. Both approaches have been shown in plant tests to improve decontamination from Zr-Nb. Also, carryover of MnO_2 into the feed solution may be decreased by improved centrifugation of the cake in the more dilute, less viscous solutions. Concentration of the feed as required for solvent extraction would be performed after the strike. Operation in this manner should remove most Zr-Nb from the solution, while the current mode of operation is much less effective in this respect.

ACKNOWLEDGMENT

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