STABILITY OF COMPLEXED ROVER DISSOLVER SOLUTIONS CONTAINING
HIGH CONCENTRATIONS OF NIOBIUM, FLUORIDE-ION, AND ALUMINUM

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ABSTRACT

The process for recovering uranium from nuclear rocket (Rover) fuels results in a complex and highly corrosive dissolver solution consisting of 2 molar nitric acid and 8 molar hydrofluoric acid. The excess fluoride must be complexed to prevent excessive corrosion. The stability ranges of the various components in the dissolver solution were investigated experimentally, and stability correlations were based on the experimental results.

SUMMARY

The processing of nuclear rocket (Rover) fuels requires high concentrations of hydrofluoric acid and nitric acid in the dissolver solution to dissolve the uranium and niobium. The resulting dissolver solution is highly corrosive and requires the addition of aluminum nitrate to complex the "free fluoride" and reduce corrosion on stainless steel processing equipment located downstream from the dissolver. The dissolver solution is very sensitive to aluminum nitrate addition; excessive aluminum nitrate results in precipitation of Nb_2O_5 . Insufficient aluminum nitrate results in precipitation of AlF_3 , and the solution remains corrosive.

The stability range of the complexed dissolver solution is narrow and time dependent. The stability range was determined experimentally to vary from 24-30% for a 2-hour period and from 0-10% for a 24-hour period. The stability range is increased to 40% over a 5-day period when the solution is diluted and adjusted for solvent extraction feed.

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I. INTRODUCTION

A combustion-dissolution process for recovering uranium from nuclear rocket (Rover) fuel has been developed at the Idaho Chemical Processing Plant (ICPP)⁽¹⁾. During the combustion step, the uranium is converted to U_3O_8 , the niobium is converted to Nb_2O_5 , and a nitric acid insoluble uranium-niobium complex, Nb_3UO_{10} , is formed in varying amounts up to 15%. During the dissolution step, hydrofluoric acid and nitric acid are required to dissolve the Nb_3UO_{10} . This combination of acids results in a complex and highly corrosive dissolver product containing various components that have limited solubility in the solution matrix and fluoride ions that must be complexed to prevent excessive corrosion of processing equipment located downstream from the dissolver. The dissolution flow-sheet proposed for the Rover plant is shown in Figure 1.

Complexing the dissolver solution to reduce its corrosion potential is a crucial step in the proposed Rover process because of the narrow concentration range of Al, the complexing agent, for which the solution does not form a precipitate. The addition of too much aluminum causes a "break" in the niobium-fluoride complex resulting in the precipitation of Nb_2O_5 . If insufficient aluminum is added, the solution remains corrosive, and the high ratio of fluoride to aluminum causes AlF_3 to precipitate.

The uranium and niobium concentrations of the dissolver solutions were varied widely during experiments. Niobium concentration greatly influenced the solution stability, whereas uranium concentration did not. Stability studies were conducted at nearly uniform experimental conditions. The dissolver solutions were maintained at the temperatures anticipated for actual plant operations; hence, they were not studied over wide temperature ranges.

Terminology:

A stable dissolver solution, as referred to in this report, is one in which no precipitate is formed over a specified time period following complexing. Stability with respect to a given component means that a particular component does not precipitate from the dissolver solution over a specified time period.

The stability range of a dissolver solution refers to the concentration range of aluminum (introduced as $\text{Al}(\text{NO}_3)_3$) for which a given dissolver solution remains stable with respect to all its components. The stability range is expressed in percent, based on the aluminum concentration of a perfectly complexed solution. The stability range is dependent upon the Nb concentration in the dissolver solution.

The stability region for purposes of this report is the area between curves generated by tracing stability-range limits over various niobium concentrations in the dissolver solution.

II. COMPLEXING ROVER DISSOLVER SOLUTIONS

A fluoride electrode was used to determine the quantity of complexing solution, $\text{Al}(\text{NO}_3)_3$, required to complex the dissolver solutions. The fluoride electrode measures the change in electrical potential of uncomplexed fluoride ions in an aliquot of dissolver solution during titration with $\text{Al}(\text{NO}_3)_3$. The electrical potential measured by the electrode is, therefore, proportional to the fluoride-ion concentration.

A typical titration curve generated by the fluoride electrode while complexing 6 ml of dissolver solution is shown in Figure 2. This curve depicts the potential change associated with an aliquot of dissolver solution when titrating with 2.2 M aluminum nitrate. The curve shows a definite break point (end point) indicating the amount of complexing solution required to complex an aliquot of dissolver solution.

The niobium concentration of dissolver solutions was used as a complexing guide in early development work, but was found to be inadequate. The niobium concentration indicates only how much fluoride is complexed with the niobium, but gives no indication of the actual fluoride-ion concentration in the overall solution matrix. It was demonstrated, as shown in Figure 3, that actual Rover dissolver solution requires more complexing than do standards of the same niobium concentration using niobium concentration as a guide. The fluoride electrode gives the precise amount of $\text{Al}(\text{NO}_3)_3$ required for complexing.

III. STABILITY OF COMPLEXED DISSOLVER SOLUTIONS

The stability of the Rover dissolver solutions with respect to uranium, nuclear poisons, AlF_3 , and Nb_2O_5 was evaluated. Analyses verified that no significant quantities of uranium or nuclear poisons were present in the precipitated solids formed as a result of over or undercomplexing dissolver solutions. That is, the Rover dissolver solutions were stable with respect to uranium and nuclear poisons for all solutions studied.

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Figure 2. Titration Curve for Complexing Fluoride with Aluminum in a Complex Matrix

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Figure 3. Complexing the Dissolver Solution Using Niobium Concentration as a Guide

Stability ranges varying from 0 to $\pm 5\%$ as shown in Figure 4, were determined for complexed standard (synthetic) Rover dissolver solutions, based on a 24-hour period following complexing. The stability ranges for the same solutions after a 2-hour period following complexing were $\pm 12\%$ to $\pm 15\%$ as shown in Figure 5. The region above the stability region in both figures represents those conditions which cause Nb_2O_5 to precipitate. The region below the stability region represents those conditions which cause AlF_3 to precipitate. Three actual Rover samples were tested and found to be in the same range as the standards for both figures. For a Nb concentration of 9 g/liter, experimental data indicate that the stability range is time dependent, as shown in Figure 6.

The amount of precipitate formed in complexed dissolver solutions for various degrees of complexing is shown in Figure 7. Three solutions containing different concentrations of niobium were used. Each solution was complexed with various quantities of aluminum nitrate, and the amount of precipitate was measured after a 24-hour settling period following complexing. Overcomplexing (too much Al) and undercomplexing (not enough Al) curves at three different levels of niobium concentration are shown in Figure 7. The figure shows that the more niobium a sample contains, the more solids the sample will generate when the solution is overcomplexed; the quantity of solids precipitated in the undercomplexed solutions is independent of Nb concentration. It can also be seen from Figure 7 that solutions containing more niobium require less aluminum for complexing.

Solids concentration in overcomplexed and undercomplexed dissolver product is shown in Figure 8 as a function of time. The solids formation rate begins slowly, increases, and finally decreases as the system approaches steady state.

The time period over which the complexed dissolver solution remains stable was increased by 25-50% and the amount of solids decreased 20-30% by adding $\text{Zr}(\text{NO}_3)_4$ to the dissolver solution. However, it is not practical to add this compound to the dissolver solution in the process.

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Figure 4. Stability Region of Complexed Rover Dissolver Solution for 24-Hour Period

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Figure 5. Stability Region of Complexed Rover Dissolver Solution for
2-Hour Period

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Figure 6. Stability Range of Complexed Rover Dissolver Solution with Respect to Time

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Figure 7. Amount of Solids Precipitated within 24-Hours of Complexing as a Function of Aluminum Concentration.

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Figure 8. Solids Formation as a Function of Time in Overcomplexed Dissolver Solution

IV. STABILITY OF "FEED-ADJUSTED" COMPLEXED DISSOLVER SOLUTION

The stability range of the complexed dissolver solutions is approximately 24-30% for a 2-hour period following complexing; the range is decreased to 0-10% for a 24-hour period following complexing. When the complexed dissolver solution is diluted 3:1 with a "feed-adjustment" solution of water and acids as shown in stream 13 of Figure 1, the stability of the solution is increased to a minimum of 40% for a five-day period as shown in Figure 9.

The dashed line in Figure 9 represents exactly complexed solutions. The area above the dashed line within the two curves is the overcomplexed stable region. The smaller area under the dashed line within two curves is the undercomplexed stable region. Since the mid-point of the stability range lies in the overcomplexed area, undercomplexing is less likely to occur than overcomplexing.

Overcomplexing is desired because of the corrosion potential existing in the undercomplexed solutions.

Three actual rover ash samples were studied and found to have the same stability ranges as the standards. All studies were based on the flowsheet conditions given in Figure 1.

V. CONCLUSIONS

The highly corrosive and complex Rover dissover product can be accurately complexed using the fluoride electrode to determine the correct quantity of $\text{Al}(\text{NO}_3)_3$ required for complexing the solution. The stability ranges for complexed dissolver solutions are approximately 24-30% for a 2-hour period and 0-10% over a 24-hour period. The stability range is increased to approximately 40% for a five-day period when the complexed dissolver solution is combined with the "feed-adjustment" solution within two hours after complexing.

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Figure 9. Stability Region of the Feed-Adjusted Complexed Dissolver Solution

The recommended procedures for complexing Rover dissolver solutions to obtain the most stable conditions are:

- (1) Complex an aliquot of the dissolver solution with aluminum nitrate reagent using the fluoride electrode to obtain an endpoint.
- (2) Determine the amount of aluminum required to obtain stability by using the value of that endpoint as the abscissa.
- (3) Complex the dissolver solution using the quantity of aluminum nitrate reagent determined from the complexing curve.
- (4) Separate the undissolved solids from the dissolver solution within 2 hours.
- (5) Combine the complexed dissolver solution with the feed adjustment solution as soon as possible following separation of undissolved solids.
- (6) Charge the resulting solutions to the extraction columns.

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