Progress Report for the Period January 1 - September 30, 1960
ORNL Subcontract No. 1327
EXTRACTION OF FUEL REPROCESSING METALS WITH ALKYL AMINES IN NITRATE SYSTEMS
MIT Nuclear Engineering Department

MITNE-6
EQUILIBRIUM EXTRACTION CHARACTERISTICS
of
ALKYL AMINES AND NUCLEAR FUELS METALS
in
NITRATE SYSTEMS

Progress Report for the Period
January 1 - September 30, 1960

Progress Report VII
by
Edward A. Mason
Richard E. Skavdahl
November 1, 1960

Work Performed Under Subcontract No. 1327
Under Contract No. W - 7405 - Eng - 26
with
Union Carbide Nuclear Company
Division of Union Carbide Corporation
Oak Ridge, Tennessee

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Cambridge 39, Massachusetts
# Table of Contents

**TEXT** | **Page**
---|---
1.0 Summary | 1
2.0 Stainless Steel Metals Progress | 2
3.0 Effect of Temperature on Zirconium Extraction | 9
  3.1 The Extraction Ratio | 9
  3.2 The Equilibrium Constant | 10
  3.3 Amine Degradation | 11
4.0 Ruthenium Progress | 14
  4.1 Literature Search | 14
  4.2 Methods of Solution Preparation | 15
    4.2.a Nitrato Complexes | 15
    4.2.b Nitro Complexes | 16
  4.3 Proposed Plan of Attack | 16
  4.4 Equipment Specification and Purchase | 17
5.0 References | 20

**FIGURES**

1. Extraction of Iron (III) | 4
2. Extraction of Cobalt (II) | 5
3. Extraction of Nickel (II) | 6
4. Extraction of Chromium (III) | 7
5. Effect of Nitrate Concentration on Stainless Steel Metals Extraction | 8
6. Zirconium Equilibrium Ratio | 12
7. Zirconium Equilibrium Constant | 13
8. Nitrosylruthenium Nitrato Complexes in Nitric Acid | 18
9. Tetra- and Penta-nitrosylruthenium Nitrato Complexes in Nitric Acid | 19
1.0 Summary

During this period, the work by Victor Vaughn has been completed and his final report is currently being finished with regard to typing and reproducing.

Two other programs have been completed: the stainless steel metals extraction studies and the effect of temperature on zirconium extraction. The species studied in the former were iron (III), cobalt (II), nickel (II), and chromium (III). These were in a nitric acid aqueous solution. At a constant initial aqueous metal concentration of about 50 gm/l and a constant initial amine concentration of about 0.3 molar, the effect of amine type (primary, secondary, and tertiary), hydrogen ion concentration, and nitrate ion concentration on the extraction ratio has been investigated. Four amines were used for the study: (1) Trilauryl amine (TLA), a straight chain tertiary amine; (2) Di (tridecyl) amine (DTDA), a straight chain secondary amine; (3) Amine S-24, a branched chain secondary amine; and (4) Primene JMT, a branched chain primary amine. Toluene was used as the diluent for the entire study.

The results of the study showed that the stainless steel metals are not extracted to any significant degree by the amines considered from aqueous nitrate systems. Extraction ratios of $10^{-5}$ are typical for these metals.

Experimental work on the temperature effect on zirconium extraction has shown an activation energy of approximately 1 to 2 KCal/mole for S-24 in Amsco or toluene and unpurified TLA in Amsco. The activation energy is about 5 KCal/mole for purified TLA in toluene. Temperature effects are slight. The value of $E_A$ being less than a factor of two greater at 50°C than at 20°C. Severe amine degradation occurs at 50°C in 8M HNO$_3$.

The ruthenium program has thus far consisted of an extensive literature search on ruthenium chemistry and solvent extraction, equipment specification and purchase, methods of solution preparation, and a proposed plan of attack.

The literature search yielded conflicting conclusions as to the extractable ruthenium species in nitric acid solution. Two systems, the nitrate-nitrosylruthenium complexes and the nitro-nitrosylruthenium complexes, were chosen as the species to be studied under varying acid, salting, and extractant conditions. Methods of solution preparation for the two systems were found.

Tracer $^{106}$Ru will be used in the investigations, so a scintillation counting set-up has been specified and purchased. In order to facilitate more rapid and reproducible titrations, a recorder and automatic constant rate burette have been purchased to go along with the existing pH meter.
2.0 Stainless Steel Metals Program

The program covering the extraction studies of the stainless steel metals iron, cobalt, nickel, and chromium has been completed and is described in detail in reference (1). A synopsis, including pertinent graphs, is described in this report.

In general, the program consisted of investigating the equilibrium extraction characteristics of Fe(III), Co(II), Ni(II), and Cr(III) by alkyl amines in nitrate systems using the four different amines JMT, TLA, S-24, and DTDA. Each metal was studied with regard to amine type, nitric acid concentration, and salt concentration. Extraction ratios were determined at initial nitric acid concentrations of approximately 2N, 6N, 8N, and 2N with added NaNO₃ to make the total nitrate concentration approximately 7N. To cover the range most important from a process point of view, the acid concentrations used span those in which uranium shows maximum extraction. By adding NaNO₃ to one of the 2N acid solutions, the effect of nitrate content at constant acid strength could be studied.

The results of this study show that with the metals cobalt, nickel, and chromium, Primene JMT extracted to a higher degree than the other three amines, reaching values for the extraction ratio of $10^{-4}$ for cobalt and nickel. With chromium, Primene JMT produced values of $E^{0}$ of $10^{-5}$, whereas the other amines extracted at $10^{-5}$ or less. In general, an increase in nitrate concentration brought about an increase in the extraction ratio. The data showing the effect of salting with NaNO₃ has been plotted in Figure 5.

Following is a description of the extraction results obtained for each individual metal.

1. Iron (III) The results for iron shown in Figure 1 seem to follow the pattern that the order of decreasing extraction was tertiary amine, secondary amine, and primary amine.

The highest extraction ratio obtained was $2.3 \times 10^{-5}$ for TLA at an initial aqueous acid concentration of 6N. A peak extraction occurs in the acid range of 4N to 6N.

The secondary amines seem to follow the same extraction pattern. Maximum extraction ratios obtained for these amines in the acid range of 2N to 8N were $1.4 \times 10^{-5}$.

The primary amine exhibited a slight decrease in extraction with increasing acid concentration. Extraction ratios of $0.7 \times 10^{-5}$ were obtained.
2. **Cobalt (II)** As shown in Figure 2, all four amines seemed to show a peak extraction in the acid range 4N to 6N. JMT gave an extraction ratio of about $2 \times 10^{-4}$ at 6N initial acid concentration in the aqueous phase.

Amine S-24 and TLA gave almost the same extraction ratios over the acid range studied, reaching maximum values of $E_A^0$ of $10^{-5}$.

DTDA had somewhat lower values with a maximum of $0.7 \times 10^{-5}$.

3. **Nickel (II)** Of the four amines studied, only JMT gave any indication of extracting nickel. See Figure 3. In this case, the value of $E_A^0$ increases steadily over the acid range studied from a value of $0.2 \times 10^{-4}$ at 2N acid to $2.5 \times 10^{-4}$ at 8N nitric acid. These results can be expressed by the following empirical equation:

$$E_A^0 = 5.32 \times 10^{-6} e^{0.21(HNO_3)}$$

where $(HNO_3)$ is the acid normality.

The method for analysis of nickel (dimethylglyoxime method) is sensitive down to about 5 μgm of nickel, which would correspond to an extraction ratio of $6 \times 10^{-6}$. However, no trace of nickel could be detected as having been extracted by the secondary and tertiary amines.

4. **Chromium (III)** This metal was extracted to an order of $10^{-5}$ by the primary amine with a maximum $E_A^0$ of $2 \times 10^{-5}$ at 6N HNO$_3$. See Figure 4. The other three amines gave extraction ratios of less than the secondary amines. All four amines seem to have a peak extraction between the acid concentration of 4N to 6N.

The "Theoretical Curves" in Figure 4 are estimates of the shape of the actual curves since the values were not obtainable at 2N and 8N because of lack of sensitivity of analysis.

All studies were at 25°C, metal concentration of approximately 50 gm/liter, and amine concentration of about 0.3 M.
EXTRACTION OF IRON(III)

$E_2^0$ vs $\text{HNO}_3$ Concentration

Legend
- PJM
- TLA
- S+24
- EDTA
- NaNO$_3$ added

Figure 1.
EXTRACTION OF COBALT (II)
$E_a$ vs $\text{HNO}_3$ Concentration

Legend:
- @ FJMT
- □ TLA
- ▲ S-24
- ◊ EDTA
- ☆ NaNO$_3$ added

$\text{HNO}_3$ Concentration, N
Figure 3

Extraction of Nickel (II)

$E_a$ vs $\text{HNO}_3$ Concentration

Legend:
○ JMT
○ JMT, NaNO$_3$ added
Figure 4.

Extraction of Chromium(III)

$E_a^0$ vs $HNO_3$ Concentration

Legend
- @: TMA
- U: TLA
- U: S-24
- @: DTBA
- A: NaN$_3$ added

--- Theoretical Curve
EFFECT OF NITRATE

\( E^e_\text{a} \) vs \( \text{NO}_3^- \) concentration

**Legend**

- C: PMT
- D: TLA
- S-24
- D14A

**Figure 5**

**SEMLOGARITHMIC**

359-73

C: CYCLES X 140

\[ \text{NO}_3^- \text{ CONCENTRATION} \]
3.0 Effect of Temperature on Zirconium Extraction

The program covering the extraction studies on the temperature effect on zirconium extraction has been completed and is described in detail in reference (2). A summary, including plotted results, is given here.

The general purpose of this program was twofold: (1) to find the dependence of $E_A^0$ on temperature, and (2) to find the effect of temperature on possible amine degradation or interaction with nitric acid.

3.1 The Extraction Ratio

In the first case, extraction studies were carried out on zirconium between the temperatures 25°C and 50°C. The extractants used were a secondary amine (S-24) and a tertiary amine (TLA). Two diluents were used, toluene and Amsco. The variable was temperature and the parameter was the extractant-diluent system.

The solutions used were:

- Aqueous solution - 5 gm/l of zirconium in 8N HNO₃
- Organic solutions - 0.301 M S-24 in Amsco
  - 0.291 M S-24 in toluene
  - 0.293 M Technical grade TLA in Amsco
  - 0.315 M Purified TLA in toluene

Ten per cent primary decyl alcohol was added in Amsco to prevent third phase formation.

The analysis for zirconium was carried out by an indirect method using a spectrophotometer.

The results of the investigation show little temperature effect on zirconium extraction, the value of $E_A^0$ being less than a factor of two greater at 50°C than at 20°C. The results, plotted as $E_A^0$ vs. $1/T$, are shown in Figure 6.

Three of the four systems show essentially the same trend, or slope, on the plot, though different absolute magnitudes. The one system that does not follow the pattern is the purified TLA-toluene system. This is thought to be because the purified TLA contains essentially no lower (secondary or primary) amines and that the plot shows the effect of temperature on TLA-toluene-zirconium extraction alone. On the other hand, the TLA-Amsco system also contains small amounts of the lower amines, so is really a plot of a mixture of extractants, not a plot of TLA.
It can be seen that the effect on S-24 is very slight, whereas that on TLA is comparatively larger. Therefore, addition of lower (primary and secondary) amines at the higher temperatures should lower the value of $E_A^0$ and the addition of lower amines at lower temperatures should raise $E_A^0$. This is qualitatively verified by the graph.

3.2 The Equilibrium Constant

Mason and Vaughen (3) defined the chemical equilibrium constant for zirconium extraction by the following equation:

$$K = \frac{E_A^0}{[A]^{1.6} [H^+]^2 [NO_3^-]^2}$$

where $[A]$ = amine molarity in organic phase
$[H^+]$ = hydrogen molarity in aqueous phase
$[NO_3^-]$ = nitrate molarity in aqueous phase

The relation between the equilibrium constant and absolute temperature is written as

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta H^0}{RT^2}$$

Assuming $\Delta H^0$ to be constant over a small range of temperature, by integration one obtains

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^0}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]$$

In the above equations, $K$ is based on activity. If $K$ is assumed based on concentration, an analogous relation can be used

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^1}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]$$

By plotting $K$ vs. $\frac{1}{T}$, it is possible to obtain a value of $\Delta H^1$, the activation energy. From Figure 7, it is shown that $\Delta H^1$ is about 1 to 2 KCal/mole for S-24 in Amsco and toluene and TLA (unpurified) in Amsco. It is about 5 KCal/mole for purified TLA in toluene.
3.3 Amine Degradation

In order to establish whether or not the amines decomposed during the runs at the higher temperature, extraction samples equilibrated at 55°C were again shaken at 25°C and the data were compared with the original 25°C values. The difference was slight, though noticeable, as can be seen from Figures 6 and 7.

The additional observations were made:

1. The organic phase was colored after it was shaken at 55°C.

2. When the organic samples of (TLA in toluene, shaken at 55°C) and (TLA in toluene, shaken at 55°C and 25°C) were titrated with sodium hydroxide solution, the color of the solution changed to yellow at the first end point of the titration curve.

This color formation is considered to be the result of the reaction of amine with nitric acid. (4)(5)(6)
FIG 6

Zt Equilibrium Ratio

△ TIA in Amoco
▼ TIA in Toluene
● S-24 in Amoco
○ S-24 in Toluene
✓ Degradation Test
FIG 7

Zr Equilibrium Constant

- TLA in Ansco
- TLA in Toluene
- S-24 in Ansco
- S-24 in Toluene

Degradation Test

\[ \frac{1}{T} \]

\[ 3.0 \quad 3.1 \quad 3.2 \quad 3.3 \times 10^{-3} \quad 1/°K \]

\[ 10^{-5} \]

\[ 10^{-6} \]
4.0 Ruthenium Progress

The ruthenium program has thus far consisted of an extensive literature search on ruthenium chemistry and solvent extraction, equipment specification and purchase, methods of solution preparation, and a proposed plan of attack.

4.1 Literature Search

The literature search on ruthenium chemistry and solvent extraction has yielded a variety of opinions as to the "extractable" and "non-extractable" forms of ruthenium in nitric acid solution. A thorough study on ruthenium extraction, which includes all known and postulated forms and species of ruthenium complexes, has apparently not been carried out. There is some quantitative data available on the extraction of a selected form of ruthenium and in selected extraction systems. In particular, some work has been done on the extraction into tributyl phosphate (TBP) of tri-valent ruthenium nitrosyl nitrato complexes in nitric acid media (7).

The variety of conclusions in the literature as to the form of the extractable and non-extractable species is evident. Zvyaginster (8) says that the extractable form is the bi-valent nitrosyl ruthenium complexes, Brown and co-workers (9) and workers at Savannah River Laboratory (10) say that it is the tri-valent nitrosyl ruthenium complexes, and Bruce (11) says that it is the higher, or tetra-, hexa-, and/or octa-valent states that are extractable.

However, extensive work by Fletcher, Brown, and others at Harwell (12-18) indicate that the important species in nitric acid solution are the nitrato- and nitro-nitrosyl ruthenium complexes. It is believed that some portion of these species contain the "extractable" form(s) of ruthenium.

The general forms of the complexes are:

Nitro-complexes: \( [\text{RuNO(NO}_2)_x\text{OH}_y\text{H}_2\text{O}_z]^{+3-(x+y)} \)

where \((x+y+z) = 5\), since Ru has a coordination number of six.

Nitrato-complexes: \( [\text{RuNO(NO}_3)_x\text{OH}_y\text{H}_2\text{O}_z]^{+3-(x+y)} \)

where again \((x+y+z) = 5\).
and a mixture: $\sum \text{RuNO(NO}_2\text{)}_w\text{(NO}_3\text{)}_x\text{(OH)}_y\text{(H}_2\text{O)}_z^{-3-(w+x+y)}$

where $(w+x+y+z) = 5$.

A plot showing the equilibrium concentration of the nitrato-complexes as a function of nitric acid concentration is given in Figure 8. (18)

The groups A, B, C, and D refer, respectively, to the mono-, di-, tri-, and tetra-plus-penta-complexes; i.e.

- $A = \sum \text{RuNO(NO}_3\text{)(H}_2\text{O)}_4^{-2}$
- $B = \sum \text{RuNO(NO}_3\text{)}_2\text{(H}_2\text{O)}_3^{-1}$
- $C = \sum \text{RuNO(NO}_3\text{)}_3\text{(H}_2\text{O)}_2^{-}$
- $D = \sum \text{RuNO(NO}_3\text{)}_4\text{(H}_2\text{O)}_7^{-1}$ and $\sum \text{RuNO(NO}_3\text{)}_5\text{)}_7^{-2}$

Figure 9 gives a breakdown of group D into the tetra- and penta-complexes separately.

Similar plots for the nitro-complexes are not yet available.

4.2 Methods of Solution Preparation

4.2.a Nitrato Complexes

The exact method of preparation of the nitrato-complexes can be found in reference (13). The general method is as follows:

1. Conversion of commercial RuCl to nitrosylruthenium chloride by passing an NO-NO$_2$ mixture into a solution of RuCl$_3$.

2. Conversion of RuNOCl$_2$ to RuNO(OH)$_3$ by boiling with addition of NaOH, maintaining pH $\geq$ 11.

3. Centrifuging at pH 6.4 to remove colloidally-suspended RuNO(OH)$_3$, after aging for several days to allow complete precipitation.
4. After drying, the \( \text{RuNO(OH)}_3 \) is dissolved and boiled in sufficient nitric acid to leave the solution about 8M HNO\(_3\). (Boiling with concentrated acid gives slow oxidation to RuO\(_4\).)

5. Evaporating solution to dryness at room temperature in a vacuum desiccator over solid caustic soda leaves the trinitrato complex as a dark red mass.

6. Dissolving in nitric acid at desired molarity and aging for several days gives the equilibrium concentrations shown in Figure 8 at the desired molarity.

4.2.5 \textbf{Nitro Complexes}

The exact method of preparation of these complexes are given in references (13) and (17). The general method is as follows.

1. Conversion of commercial RuCl\(_3\) to RuNOCI by passing an NO-NO\(_2\) mixture into a solution of RuCl\(_3\).

2. Conversion of RuNOCI to Na\(_2\)RuNO(NO\(_2\))\(_4\)OH\(_7\) by adding slowly additional NaNO\(_2\) at 80\(^\circ\)C and pH~7.

3. Conversion of Na\(_2\)RuNO(NO\(_2\))\(_4\)(OH)\(_7\) to RuNO(NO\(_2\))\(_2\)(OH)(H\(_2\)O)\(_2\)\(_7\) by addition of dilute acid.

4. Conversion of (RuNO) nitrate complexes to \( \text{RuNO(NO}_2\text{O}_2\text{)(NO}_3\text{)}_2\text{(H}_2\text{O)}_2\text{\(_7\)) and \( \text{RuNO(NO}_2\text{O}_2\text{)}_3\text{(H}_2\text{O)}_2\text{\(_7\))\text{ by evaporation in vacuo of solutions formed in nitric acid by the action of oxides of nitrogen (NO+NO}_2\text{)} on (RuNO) nitrate complexes.\}

4.3 \textbf{Proposed Plan of Attack}

The general approach in the forthcoming studies of ruthenium extraction by amine-type reagents will be to consider initially the nitrato-complexes and then the nitro-complexes. Other species may be investigated, though it does not appear at this time that the other species are of importance.

Solutions of the complexes will be prepared varying in acid concentration from about 0.1M to 12M, varying in salting concentration from zero to saturation, and varying in ruthenium concentration. These will be extracted with an organic phase which will be varied with regard to amine type (primary, secondary, tertiary, and/or quaternary), amine concentration, and possibly diluent type.
The extractions may also be varied with respect to shaking, or contact, time, especially in the case of the nitrato complexes, where rearrangement to equilibrium concentrations is faster than in the nitro-complexes.

The desired result is the knowledge of the extractable and non-extractable forms of ruthenium, the method or mechanism of extraction, and the quantitative data regarding extraction ratios of the individual species and the amount of species in solution.

The application of this knowledge would be in the prediction of the behavior of ruthenium under various process conditions and to facilitate adjusting the conditions to meet a specific purpose. For instance, one application of this work would be the specification of optimum scrubbing conditions for ruthenium decontamination.

4.4 Equipment Specification and Purchase

It is planned to use tracer Ru\textsuperscript{106} along with macro-amounts of carrier Ru in the extraction studies. The values of $E_0$ will be determined by the ratio of counting rates of equal portions of organic and aqueous phase. In order to accomplish this, a well-type scintillation counting set-up was procured.

To enable faster and more reproducible titrations, an automatic constant rate burette and a recorder for the existing pH meter has been obtained.
Nitrosyl Ruthenium Nitrate Complexes in Nitric Acid

Fig. 8


R. E. Skaugland
July 13, 1960
Nitrosyl Ruthenium Nitrate Complexes in Nitric Acid

**Fig. 9**

5.0 References


(10) "Nuclear Magnetic Resonance Spectra of N-14 in Ruthenium Nitrosyl Complexes," DP-391.


