Optimization of Some Parameters on the Low Efficiency of Solvent Extraction of Uranium with Alamine 336

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ABSTRACT

Solvent extraction of uranium from sulfate liquor acid ore with Alamine 336 from two suppliers has been studied. The influence of various parameters, such as sulfuric acid concentration on uranium bearing solutions, concentration of Alamine 336, and concentration of uranium was investigated. The decrease of uranium efficiency extraction at the plant was caused by the degradation of the organic phase. Degradation caused by the presence of vanadium in the uranium ore. Two theoretical stages could efficiency extract more than 90% of uranium from a solution containing 3881 mg/L at O/A ratio of 1.5:1. At the range of sulfuric acid concentration of 0.1 M to 0.2 M, Uranium efficiency was enhanced from 89% to 92 at the 1st contact and from 18% to 20% at the second contact. At this range of concentration, the UO$_2$(SO$_4$)$_2^{2-}$ species predominate. For sulfuric acid concentrations over 0.2 M the uranium efficiency decreased due to the presence of UO$_2$(SO$_4$)$_3^{4-}$ and UO$_2$(SO$_4$)$_4^{6-}$ species. Improving volume percentage of Alamine 336 in organic phase enhanced the uranium efficiency to 99%.

Keywords: Optimization, Solvent extraction, Uranium, Alamine 336, Niger plant.

INTRODUCTION

The production of nuclear fuel at a competitive price compared with other sources of energy is a permanent concern of the nuclear industry.

The solution of this situation must necessarily go through the research and exploitation of new uranium deposits, but also through the mastery of nuclear technology to design very safe, reliable and environment-friendly nuclear power plants.

The Republic of Niger is located in West Africa with an area of 1.267.000 km$^2$ annually produces more than 3.000 tons of uranium. In 2016, national production was 3.479 tones. So, it has
risen to the 4th position among uranium producing countries in the world. However, it remains one of the poorest countries with a GDP, which ranks it 143rd in the world on 195. Uranium constitutes the country’s main source of income in the industrial field.

The uranium sites discovered in Niger are located in the northwestern part of the country, on the western border of the Air massif. The main mining sites in exploitation are the Arlit site, the Akouta site and the Azelik site respectively exploited by SOMAÏR, COMINAK and CNNC (Chinese).

ORANO (formerly known as AREVA) is the majority shareholder of SOMAÏR and COMINAK. At the Akouta Mining Company, uranium is found in the Guezouman sandstone formations, whose mineralized can vary from 1 to 15 m with an ore concentration between 0.2% and 0.6% in uranium. The sterile cover is 250 m. These companies purify and concentrate uranium, which the final products are respectively sodium diuranate (Na$_2$U$_2$O$_7$) and magnesium diuranate (MgU$_2$O$_7$).

Generally confined in uranium ore, vanadium, zirconium and molybdenum are troublesome elements for the Republic of Niger, which prefers to valorize uranium.

These uranium companies use liquid-liquid extraction as the process to recover uranium. Tertiary amines such as Alamine 336 are widely used in the extraction of uranium.

Over the extraction cycles, the solvent loses its efficiency to extract uranium. This solvent is a mixture of Alamine 336 as extractant, isotridecanol as alcoholic modifier and kerosene as diluent. Some studies on the chemical mechanism of solvent degradation proved that the conversion of tri-n-octylamine were responsible of the low uranium rate recovering. Indeed, the presence of vanadium in the uranium bearing solutions on polyvanadates forms was majority responsible for that modification of Alamine 336. They also reported that the presence of other parameters like molecular dioxygen, chromium influenced the solvent degradation.

In this regard, we focused on the solvent extraction of uranium from uranium bearing solutions of Cominak plant. The effects of various parameters like contact number, ratio between organic and aqueous phase, uranium concentration, Alamine 336 concentration and sulfuric acid concentration were investigated in order to extract efficiency uranium.

**MATERIALS AND METHODS**

**The reactants**

Alamine 336 (industrial grade, Cognis and BASF) was an anionic extractant with a flashpoint of 179°C. Kerosene (industrial grade, Total) was used as diluent Table 1 shown some properties. Isotridecanol (analytical grade, VWR) was used to avoid the formation of the third phase with a flashpoint of 122.5°C. The mixture of these reagents formed the organic phase.

| Table 1: Kerosene properties |
|-----------------------------|
| Density (g/cm$^3$)          | 0.788 |
| Viscosity (cP)              | 1.64  |
| Solubility in water at 20°C | -     |
| Dielectric constant         | 1.8   |
| Boiling point (°C)          | 150   |
| Molecular weight (g/mol)    | 170.34|
| Flash point (°C)            | 54    |

Tri-octyl-phosphine oxide (TOPO) was a solvating or neutral extractant (purity > 99%, Merck), sulfuric acid (purity 95%, VWR), nitric acid (purity 65%, VWR), sodium fluoride (analytical grade, VWR) were used to prepare organic phase to re-extract uranium from aqueous samples. Pyridin (analytical grade, VWR), dibenzoylethane (purity>99%, Merck) were used to dose uranium.

The aqueous phases were prepared from uranium-bearing solutions, Fig.1 those last were obtained from the leaching of uranium ores process.

![Fig.1. Uranium solvent extraction process](image-url)
The solutions had a free acidity (H\(^+\)) of 10 to 22 g/L and Table 2 shown the composition of some parameters. The experimental temperature was maintained at 30°C.

| Sample                | Concentration |
|-----------------------|---------------|
| Uranium (mg/L)        | 3698          |
| Molybdenum (mg/L)     | 52            |
| Vanadium (mg/L)       | 2423          |
| Zirconium (mg/L)      | 20            |
| Iron (mg/L)           | 465           |
| pH                    | 1             |
| Redox potential (mV)  | 496           |

**Extraction procedure**

The extraction process was done in mixer-settler. The shaking was set at 700 rpm with a Heidolph brand agitator. The pH was determined with Knick pH-meter 766-calimatic device and the redox with Hanna HI 98240 pH/ORP meters device. In the mixer-settler 100 mL of aqueous phase containing the metal and 100 mL of organic phase containing Alamine 336 were brought into 2 min, sufficient time for the transfer of metal from one phase to the other. At the end of the extraction, the two phases were separated by decantation.

The analysis of the aqueous samples was done after an adequate dilution. The test samples depended on the uranium concentration in the aqueous solutions (directly for weak concentrations and by dilution for high concentrations).

In pill jar containers of 60 mL according to the test samples, the following additions were made: solution of HNO\(_3\) at 10%; solution of NaF as oxidant; solution of TOPO as extractant. The whole were stirred for 10 minutes. After decantation, the organic phase (TOPO) was carefully removed. It was taken using a diluting device. The setting was of 1 mL of the organic phase for 3 mL of the DBM solution. The formation of a U-DBM complex of yellow coloring in pyridine medium was obtained.

The uranium was analyzed with a Varian Cary 50 UV-Vis spectrophotometer at 405 nm.

The determination of molybdenum in the aqueous phase was carried out directly after an adequate dilution with solution of Al(NO\(_3\))\(_3\), solution of KCl, and solution of HNO\(_3\). Molybdenum was analyzed using a Varian AAFS240 atomic absorption spectrophotometer equipped with an acetylene-nitrous oxide burner at 313 nm.

The distribution coefficient relation of Eq. (1) and the extraction efficiency percentage relation of Eq. (2) were respectively determined by the following formulas:

\[
D = \frac{[M]_{\text{org}}}{[M]_{\text{aq}}} 
\]

\[
E(\%) = \left( \frac{D}{D + \left( \frac{V_{\text{aq}}}{V_{\text{org}}} \right)} \right) \times 100
\]

\[ [M]_{\text{org}} = \text{Metal concentration in the organic phase (mg/L)} \]

\[ [M]_{\text{aq}} = \text{Metal concentration in the aqueous phase (mg/L)} \]

**RESULTS AND DISCUSSIONS**

**Effect of Alamine 336 degradation**

In order to study the behavior of the solvent during the extraction process, Alamine 336 from two suppliers (Cognis and BASF) and Alamine 336 (Cognis) regenerated from the plant after several extraction cycles were investigated. The aqueous phase had uranium concentration of 3698 mg/L and pH = 1. The redox potential was 498 mV and the organic phase had an Alamine 336 concentration of 0.1 M in kerosene. The extraction was carried out in 5 contacts with an O/A ratio of 0.5. The results are shown in Fig. 2. The solvent formed from Alamine 336 (Cognis and BASF) exhibited the same extraction behavior. Whereas, the regenerate solvent the uranium extraction decreased. Fig. 3 shown the total amount of uranium extracted with the 3 solvents after the 5 extraction cycles. The decrease of the extraction efficiency for the regenerated solvent may be due to the loss of Alamine 336 capacity to extract uranium. Indeed, according to Chagnes\(^7\) works on the improvement resistance of solvent degradation of COMINAK plant, Alamine 336 had tended to transform into secondary amine, primary amine and other compounds. This degradation was due to the presence of powerful
oxidants in ore such as vanadium⁸ and chromium⁹. Abdoul-Rachid¹⁰ reported also that beyond 700 mV, Alamine 336 effectively extracted vanadium, which automatically caused the decrease of uranium extraction efficiency.

For following works Alamine 336 supplied by Cognis was used.

U = 3698 mg/L, Mo = 65 mg/L, V = 2370 mg/L and pH = 1. The redox potential was 498 mV and the free acidity was $\text{H}^+ = 22$ g/L. The organic phase had an Alamine 336 concentration of 0.1 M in kerosene. The extraction was carried out in 5 contacts. Fig. 4 illustrates the effect of contact number on uranium extraction efficiency. Uranium extraction was effective at the first contact with 38%. Molybdenum efficiency extraction decreased from 7% to the first contact to 3% at second contact. At 498 mV Alamine 336 did not extract vanadium. The weak extraction efficiency may be due to these parameters low phase ratio O/A, sulfuric acid concentration of uranium bearing solutions.

**McCabe Thiele isotherm**

In order to obtain the optimal contact number for the extraction, McCabe Thiele isotherm was plotted. The aqueous phase had a uranium concentration of 3881 mg/L. The free acidity was $\text{H}^+ = 12$ g/L and redox potential was 498 mV. The organic phase had an Alamine 336 concentration of 0.1 M in kerosene. The ratios O/A were varied from 1:2, 1:1, 1.5:1 and 2:1. According, to results shown at Fig. 5. Two theoretical stages were required to extract efficiency uranium from uranium bearing solutions¹¹. Collet¹² studies on computer simulation and optimization of flow sheets reported also that with two feed inlets uranium could be recovery efficiency.
In order to increase the uranium extraction efficiency between the 1\textsuperscript{st} and 2\textsuperscript{nd} contact, parameters illustrated in section 3.4 to 3.7 were studied.

Effect of the ratio of organic phase and aqueous phase

The aqueous phase contained the following metals: U = 3881 mg/L, Mo = 60 mg/L, V = 2370 mg/L. The free acidity was H\textsuperscript{+} = 12 g/L and the redox potential was 496 mV. The organic phase had an Alamine 336 concentration of 0.1 M in kerosene. The extraction was carried out in 2 contacts. The effect of O/A was shown at Fig. 6. The variation of ratio O/A increased the uranium extraction efficiency from 39.47\% up to 99.67\% at the 1\textsuperscript{st} contact and from 5.16\% up to 94\% at the second contact.

Effect of sulfuric acid concentration

The aqueous phase contained the following metals: U = 3619 mg/L, Mo = 50 mg/L, V = 2180 mg/L. The free acidity was H\textsuperscript{+} = 10 g/L and the redox potential 500 mV. The organic phase had an Alamine 336 concentration of 0.1 M in kerosene. The ratio O/A = 1:1. The sulfuric acid concentration of uranium bearing solutions was varied from 0.1 to 1 mol/L. Fig. 7 illustrates the effect of sulfuric acid concentration on uranium extraction. For low sulfuric acid concentration (0.1-0.2) in the uranium bearing solutions, extraction efficiency increased from 88.91 up to 92\% at the 1\textsuperscript{st} contact and from 18.42\% up to 20\% at the second contact. This enhancement of extraction efficiency may be due to UO\textsubscript{2}(SO\textsubscript{4})\textsuperscript{2-} species which was majority in the solution at these range of concentrations. For lower sulfuric acid concentration uranium was in its UO\textsubscript{2}(SO\textsubscript{4})\textsuperscript{2-} and UO\textsubscript{2}(SO\textsubscript{4})\textsuperscript{3-} species in uranium bearing solutions\textsuperscript{13}. In similar conditions [(R\textsubscript{3}NH\textsubscript{3})\textsubscript{4}UO\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}]\textsuperscript{-} complex was obtained during the extraction of UO\textsubscript{2}(SO\textsubscript{4})\textsubscript{2-} by Alamine 336\textsuperscript{14-15}.

The uranium extraction efficiency decreased when sulfuric acid concentrations were enhanced up to 0.2 M. Fig. 8 shown the diagram of the different uranium species present in strong sulfuric acid solutions\textsuperscript{16}. Indeed, this drop of uranium extraction efficiency may be due to the different extraction mechanism because of the different speciation of uranium UO\textsubscript{2}(SO\textsubscript{4})\textsuperscript{2-} and UO\textsubscript{2}(SO\textsubscript{4})\textsuperscript{3-} present in uranium bearing solutions. E.C Avelar\textsuperscript{17} studies on the modeling of the solvent extraction equilibrium of uranium reported that at higher concentration of sulfate ions UO\textsubscript{2}(SO\textsubscript{4})\textsubscript{3-} species were formed.

Therefore, the mechanisms of uranium extraction can described by the following equations:

\[
[(R\textsubscript{3}NH\textsubscript{3})\textsubscript{2}SO\textsubscript{4}\textsubscript{2-}]\text{org} + [UO\textsubscript{2}(SO\textsubscript{4})\textsubscript{2-}]\text{aq} \rightleftharpoons [(R\textsubscript{3}NH\textsubscript{3})\textsubscript{2}UO\textsubscript{2}(SO\textsubscript{4})\textsubscript{2-}]\text{org} + [SO\textsubscript{4}\textsubscript{2-}]\text{aq} \quad (3)
\]

\[
2[(R\textsubscript{3}NH\textsubscript{3})\textsubscript{2}SO\textsubscript{4}\textsubscript{2-}]\text{org} + [UO\textsubscript{2}(SO\textsubscript{4})\textsubscript{4-}]\text{aq} \rightleftharpoons [(R\textsubscript{3}NH\textsubscript{3})\textsubscript{4}UO\textsubscript{2}(SO\textsubscript{4})\textsubscript{4-}]\text{org} + 2[SO\textsubscript{4}\textsubscript{2-}]\text{aq} \quad (4)
\]
Effect of uranium concentration

Various industrial solutions loaded with uranium were used. Barren liquor from the second filtration with $\text{U} = 450 \text{ mg/L}$, production liquor from the first filtration with $\text{U} = 1064 \text{ mg/L}$, bearing solution with $\text{U} = 3619 \text{ mg/L}$ and uranium bearing solution from storage tank with $\text{U} = 7112 \text{ mg/L}$. The redox potential was 500 mV. The organic phase had an Alamine 336 concentration of 0.1 M in kerosene. The ratio O/A = 1 and the extraction was carried out in 2 contacts. Fig. 9 illustrates the results. The extraction was effective for uranium concentration of 1000 mg/L with efficiency percentage exceeding 90%. The drop of the uranium percentage reflected the saturation of the complexing sites of Alamine 336. This saturation may be due to also to the $\text{UO}_2(\text{SO}_4)_{3/4}^4$ speciation and 4 molecules of Alamine 336 complex one molecules of uranium sulfate according to the 1:4 stoichiometry$^{18-19}$.

Effect of volume proportion of Alamine 336 in solvent formation

The aqueous phase contained the following metals: $\text{U}=3619 \text{ mg/L}$, $\text{Mo}=50 \text{ mg/L}$, $\text{V}=2180 \text{ mg/L}$. The redox potential was 500 mV and the free acidity was $\text{H}^+=10 \text{ g/L}$.

The proportion of Alamine 336, alcohol (Isotridecanol) and kerosene were varied and were illustrated in Table 3.

| Alamine 336 percentage | Isotridecanol percentage | Kerosene percentage |
|------------------------|--------------------------|---------------------|
| 2.5                    | 3                        | 94.5                |
| 5                      | 10                       | 85                  |
| 7.5                    | 3                        | 89.5                |
| 10                     | 10                       | 80                  |

The enhancement Fig.10 of Alamine 336 proportion in the organic phase formation increased the uranium extraction efficiency from 78.72% up to 99.58% at the first contact and from 4.61% up to 95.79% at the second contact. The addition of isotridecanol prevented the formation of a third phase. Zhu$^{20}$ reported that using equal concentration percentage of isodecanol and Aliquat 336 eliminated the third phase formation.

CONCLUSION

The solvent extraction of uranium from sulfate liquor acid of Niger plant by Alamine 336 in kerosene modified with isotridecanol was investigated. The weak extractability of uranium was due to the degradation of Alamine 336, degradation...
caused by the presence of vanadium, which was an oxidant. According to McCabe Thiele isotherm, two theoretical stages were required to extract efficiency uranium. The variation of the O/A ratio from 0.5 to 2 had made it possible to recover more than 90% of uranium at the first contact. The variation in the $\text{H}_2\text{SO}_4$ concentration of the uranium liquor from 0.1 to 0.2 had also made it possible to recover more than 92% of uranium at first contact. For concentrations lower than 0.2 M the species $\text{UO}_2(\text{SO}_4)_{3-}$ was predominant while for concentrations higher than 0.2 M it had coexistence of the $\text{UO}_2(\text{SO}_4)_{3-}$ and $\text{UO}_2(\text{SO}_4)_{4+}$ species. The variation of the volume proportions of Alamine 336 and kerosene had made it possible to raise the uranium efficiency more than 98% with a volume percentage of Alamine 336 of 10 in the organic phase.

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Conflicts of Interest

The authors declare no conflict of interest.

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