Application of Solvent-In-Pulp Technique for Uranium Extraction from Mineralization Granite

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ABSTRACT

Investigations on uranium extraction from a representative mineralized granite sample (Gattar granite GII) by solvent-in-pulp (SIP) technique were carried out in the present study. For this purpose, the solvent (tri-butyl amine) (TBA) was mixed with the leaching slurry without prior filtration. The influence of various factors affecting the SIP process, such as contact time, solvent concentration, dilution factor, type of surfactant, surfactant/solid ratio were studied. About 91% uranium extraction efficiency was attained by the application of the chosen extraction SIP conditions. Also, about 96% of the loaded uranium could be stripped by using sulfuric acid as an effective stripping agent.

Keywords: Uranium/Extraction/Solvent-in-pulp

INTRODUCTION

Several uranium occurrences have been discovered in various localities in the Egyptian terrains. These include mainly the different uranium mineralization associated with younger granites of the basement rocks in the Eastern Desert or else those associated with the sedimentary Carboniferous rocks of the Um Bugma Formation in West Central Sinai. Among uranium mineralization of the former type, that occur in Gabal Gattar younger granite pluton at about 40 km NW Hurghada City is greatly promising due to its relatively wide distribution in a number of occurrences. In the north eastern part of Gabal Gattar, the younger granites host several small uranium occurrences that have been discovered along various factors, fault planes and joints that distributed in strongly sheared zones (1). The uranium mineralization is essentially manifested in the form of secondary uranium minerals with uranophane as the most abundant (2).

Solvent extraction (3-7), ion exchange resin (8) liquid membrane (9) and direct precipitation (10) methods are commonly employed in the nuclear industry as techniques for the recovery of uranium from leach solutions. To carry out this operation, special equipment was used such as mixer settlers and ion-exchange columns. The used leach solutions must be prepared and clarified since fine solids may produce stable emulsions or columns blocking which prevents phase separation and the presence of severe operational problems. However the clarifications (or filtration) operations required are expensive. According to Campbell et al. (11) the capital and operating costs for clarification processes are estimated to be 30% and 10-20% respectively of the nuclear industry. Consequently, if these operations can be eliminated by using slurries, significant investments should be achieved. This method of processing has been termed solvent-in-pulp (12) (SIP). If dilute slurries were used in SIP processing, the filtration operation would be removed.
An extensive economic study was carried out by Ritcey et al.\textsuperscript{(13)} The authors compared processing characteristics and economics of resin-in-pulp and solvent-in-pulp operations as applied to uranium extraction, and runs were carried out with continuous aqueous and organic phases. Although the process was easier to operate with the continuous organic phase, operation with the continuous aqueous phase resulted in much lower solvent losses and was consequently recommended as the favored mode of operation. Solvent losses were found to be the serious factor influencing the economics of the process. Some further investigations have been carried out to determine the factors influencing solvent losses. Ellis et al.\textsuperscript{(14)} found that losses could be substantially reduced by the addition of hydrophilic surfactants. By avoiding high losses of solvent to the particles, and removal of possibilities for crud formation, extraction and recovery of uranium directly from the leach slurry is thus proved feasible \textsuperscript{(14)}. Once uranium is in the solvent, the second operation step starts by stripping uranium from the loaded solvent. Several reagents were tested in this regard such as H$_2$SO$_4$, Na$_2$CO$_3$, HCl, HNO$_3$ and H$_2$O.

The main objective of this study is uranium recovery from Gattar granite GII by SIP technique. To achieve this purpose the effect of various factors affecting uranium extraction by the SIP technique from GII leaching slurry such as, solvent concentration, slurry dilution, shaking time, solid/liquid phase ratio, diluent type and solvent consumption (surfactant type and surfactant/ slurry ratio) were studied. The second part of the study focused on the uranium stripping from the working solvent. In this regard, several factors were studied such as stripping agent type, stripping agent concentration, shaking time and organic/ aqueous phase ratio.

**EXPERIMENTAL**

2.1. Materials

The chemical reagents that have been used in this study were of high purity Tributylamine (TBA) ≥ 98\% (Riedel-deHaen), kerosene (Misr. Co.), uranylacetate (UO$_2$(CH$_3$COO)$_2$.2H$_2$O, (BDH Chemicals Ltd. Poole, England) and Molasses (Misr. Co.), and Sulfuric acid (BDH) 98\%.

The representative sample was collected from Gabal Gattar, with the chemical composition of 1310 mg/l U, 2.11\% SO$_4^{2-}$, 1.61\% PO$_4^{3-}$, 71.51\% SiO$_2$, 0.42\% CaO, 7.01\% Fe$_2$O$_3$ and 0.06 \% TiO$_2$.

2.2. Experimental Procedure

**Working Slurry Preparation**

Proper conventional agitation leaching of studied sample was performed by sulfuric acid, based on the previous studied leaching conditions of Mahfous\textsuperscript{(15)}. These included 30 kg/t sulfuric acid, 1/5 solid/liquid ratio, -35 mesh grain size and the leaching was performed for 4 h agitation time at room temperature. Analysis of the obtained leach slurry (pH 1.1) revealed an assay of 1280 mg/l for uranium and 46.0 g/l for SO$_4^{2-}$. Under the latter mentioned preferred conditions, about 97.67\% uranium leaching efficiency was attained.

**Uranium Extraction**

The influence of various factors affecting uranium extraction by the SIP technique from GII leaching slurry such as, solvent concentration, slurry dilution, shaking time, solid/liquid phase ratio, diluent type and solvent consumption (surfactant type and surfactant/ slurry ratio) were studied.

**Uranium Stripping**

The effect of several factors affecting uranium stripping from TBA namely, stripping agent type, stripping agent concentration, shaking time and organic/ aqueous phase ratio were investigated. For this purpose a loaded TBA sample (0.978 gU/l) was proper prepared by accumulative uranium extraction from the leach slurry.
2.3. Analytical Method

Uranium was analyzed in the corresponding aqueous phases under different conditions (16) using Arsenazo III reagent. For this purpose, a Lambda UV/VIS spectro-photometer (Perkin-Elmer, USA) was used.

2.4. Equilibration Calculation

All uranium speciations in this study were achieved with Hydra-MEDUSA, a chemical equilibrium calculation program (17).

RESULTS AND DISCUSSION

3.1. Relevant Factors of Uranium Extraction from Gattar Granite GII Sample Using SIP Method

3.1.1. Effect of Solvent Concentration

To study the effect of tri-butyl amine (TBA) solvent concentration on uranium recovery from the study sample leaching slurry uranium conc., 1280 mg/l, series of extraction experiments were performed by contacting fixed slurry portions (20 ml) with the solvent of different concentrations ranged from 0.05 to 1.06 M (1 - 20%) in benzene. The other conditions were fixed, namely, dilution factor of 230 g solid/l, shaking time of 15 min. and solvent/liquid phase ratio of 1/1. After separation of the two phases, uranium was determined in the aqueous phase and thereupon the extraction efficiency was calculated by the different. From the obtained results, (Fig. 1), it was clearly obvious that uranium extraction efficiency increases with increasing the solvent concentration. On the other hand, one could observe that the loss of solvent ratio decreased slightly by increasing its concentration.

![Fig. (1): Effect of solvent concentration on uranium extraction efficiency from Gattar Granite GII sample (dilution factor of 230 g solid/l, shaking time of 15 min., solvent/liquid phase ratio of 1/1 and slurry pH of 1.1)](image)

3.1.2. Effect of Dilution

In order to study the effect of the dilution factor of the leaching slurry on uranium extraction, a series of experiments were performed by contacting fixed slurry portions (20ml) of uranium conc., 1280 mg/l with different solid contents (weight of solid in slurry solution) ranging from 102 up to 230 g solid /l by adding water to original leaching slurry. It is important to mention, that the uranium concentration has been justified in every sample by adding desired volumes of uranium standards. The other conditions were fixed namely; solvent concentration of 20%, shaking time of 15 min and solvent/liquid phase ratio of 1/1. The obtained results show that uranium extraction efficiency decreased from about 56 down to 26%) by increasing the solid content from 102 to 230 g/l
respectively (Fig. 2), and the solvent loss increased from 5 up to 17 % of solvent by increasing the solid content. The decrease of uranium extraction efficiency with the increase of the solid content could be attributed to the increase of solid particles which inhibit the free motion of the solvent molecules in the matrix. On the other hand, the increase in solvent loss could be attributed to absorbing the solvent molecules on the surface of the thick gangue of mineral particles.

Fig. (2): Effect of solids concentration upon uranium extraction efficiency from Gattar Granite GII sample (Solvent conc. of 20% in benzene, shaking time of 15 min., solvent/liquid phase ratio of 1/1 and slurry pH of 1.1)

3.1.3. Effect of Shaking Time

To study the effect of shaking time upon uranium extraction efficiency from Gattar GII granite sample, series of extraction experiments were performed by contacting fixed slurry portions (20 ml) of uranium conc. of 1280 mg/l with the solvent using time intervals ranging from 1 up to 120 min. Other conditions were fixed namely, solids conc. of 102 g/l, phase ratio of 1/1 and solvent concentration of 20%. The obtained results could indicate that uranium extraction efficiency increases with increasing shaking time (Fig.3) while solvent loss was nearly unaffected. Accordingly, it was decided to choose 60 minute as the optimum shaking time.

Fig. (3): Effect of shaking time upon uranium extraction efficiency from Granite GII sample (Solvent conc. of 20% in benzene, solids conc. of 102 g/l, solvent/liquid phase ratio of 1/1 and slurry pH of 1.1)
3.1.4. Factors Affecting Solvent Loss

Successful SIP extraction operation of uranium from the obtained leach slurry will be measured by the extraction efficiency as well as by the lost amount of solvent. Accordingly, non-ionic hydrophilic organic material e.g. molasses, glue, crud sugar and hydrophobic organic surfactant e.g. vegetable oil were tested. These reagents were added to the leach slurry to minimize or prevent solvent adsorption losses on the ore and gangue particles in the subsequent extraction process.

3.1.4.1. Effect of Surfactant Type

To study the effect surfactant type upon uranium extraction, various types were tested, mainly; molasses, glue, crud sugar and vegetable oil. The experiments were performed by mixing 0.5 g of each surfactant with the slurry portions (20 ml of slurry with uranium conc. of 1280 mg/l) for 30 min prior to contact them with the solvent. The solvent loss is calculated by the difference in weight before and after the contact. Other factors were fixed at a solvent concentration of 20%, solid content of 102 g/l for 60 min. contact time and solvent /slurry ratio of 1/1. The results show that the higher uranium extraction efficiency (about 60%) was obtained by using glue as an effective surfactant (Fig. 4).

![Fig. (4): Effect of surfactant type on uranium extraction efficiency and solvent loss (Solvent conc. of 20% in benzene, solids conc. of 102 g/l, shaking time of 60 min., solvent/liquid phase ratio of 1/1 and slurry pH of 1.1)](image)

3.1.4.2. Effect of Surfactant Amount

To investigate the effect of surfactant amount upon the uranium extraction efficiency, a series of extraction experiments were performed by contacting fixed slurry portions (20 ml of slurry with uranium conc. of 1280 mg/l) with the surfactant proper mixing with the solvent. For this purpose, different amounts of glue, ranging from 25 up to 200 g/l were added and agitated with the slurry before solvent. Other factors were fixed at solvent concentration of 20 % TBA, shaking time of 60 min. and solid amount of 102 g/l. From the obtained data (Fig. 5) it could be observed that by increasing the surfactant (glue) amount led to a noticeable decreases solvent loss. In the same time, uranium extraction efficiency increased with increasing the former glue amount.
Fig (5): Effect of surfactant amount upon uranium extraction efficiency and solvent loss (Solvent conc. of 20% in benzene, solids conc. of 102 g/l., shaking time of 60 min., surfactant type of glue and slurry pH of 1.1)

3.1.5. Effect of Slurry/Organic Phase Ratio

In order to identify the effect of diluted slurry/organic phase ratio upon uranium recovery, a series of extraction experiments were performed by contacting the diluted slurry with TBA solution in benzene (20 ml of slurry with uranium conc. of 1280 mg/l) using different ratios ranging from 0.5/1 up to 4/1. These experiments were performed under fixed conditions of solvent concentration of 20 % TBA for 60 min. contact time, solid content of 102 g/l and 100 g/l of glue. It is noticed that the uranium extraction efficiency increases with the increase of the phase ratios (Fig. 6). Increasing uranium extraction efficiency in association with increasing the phase ratio could be explained in relation to the decrease in the viscosity of the slurry, a matter which could enhance uranium extraction efficiency (as shown in the last experiment of 4/1 A/O ratio). On the other hand, the solvent loss (consumption) decreased by increasing slurry/organic phase ratios as shown in the last experiment.

Fig. (6): Effect of aqueous/organic phase ratio upon uranium extraction efficiency and solvent loss (Solvent conc. of 20% in benzene, solids conc. of 102 g/l., shaking time of 60 min., surfactant type of glue, surfactant amount of 100g/l and slurry pH of 1.1)
3.1.6. Effect of Diluent Type

In order to identify the effect of diluent types on the uranium extraction efficiency of the diluted leaching slurry from Gattar GII granite sample, different diluents were tested namely; benzene, toluene, cyclohexane and kerosene. Different solvent sample diluted by the previous diluents were contacted with different slurry portions (20 ml each) with fixed uranium concentration of 1280 g/l. Other factors were fixed at solvent concentration of 20% TBA, for 60 min contact time, solid content of 102 g/l, surfactant amount of 100 g/l (glue) and slurry/organic phase ratio of 4/1. The obtained data shows that benzene and kerosene gave nearly equal ratios of the maximum uranium extraction efficiency and minimum solvent loss (Fig. 7). Based on the economic considerations, we recommend kerosene as diluent.

![Uranium extraction efficiency and Solvent loss vs Diluent type](image)

**Fig. (7):** Effect of diluent type on uranium extraction efficiency from Gattar granite GII composite sample (Solvent conc. of 20% in benzene, solids conc. of 102 g/l., shaking time of 60 min., solvent/liquid phase ratio of 4/1, surfactant type of glue, surfactant amount of 100g/l and slurry pH of 1.1)

3.1.7. Choice of the Preferred Conditions of Uranium Extraction from Gattar Granite GII Sample

From the previous study of relevant factors of uranium extraction, it would be possible to attain comparable extraction efficiencies by different combinations of the studied relevant factors. Careful selection of the conditions would depend primarily on economic considerations. In the light of the studied relevant factors, it would seem economically to select the following extraction conditions, solvent concentration of 20%, extraction time of 60 min, solid content of 102 g/l, glue as surfactant of 100 g/l, slurry/organic phase ratio of 4/1 and using kerosene as the diluent substance.

3.2. Amine/Uranium Extraction Mechanism

When considering amine extraction systems, the amine salt should be regarded as the extracting agent, rather than the free amine itself. The amine is firstly converted to the appropriate amine salt:

\[ \text{RH}_2\text{N} + \text{HX} = \text{RH}_2\text{N}^+\text{H}^- \]  \hspace{1cm} (1)

The amine is forms with an acid (HX) – in the organic phase – amine salt (or polar ion-pair), \( \text{RH}_2\text{N}^+\text{H}^- \). On contacting this solvent with an aqueous solution of an ionic metal species (MY\(^-\)), the exchange occurs according to the following equation\(^{18-20}\):

\[ \text{RH}_2\text{N}^+\text{H}^- + \text{MY}^- = \text{RH}_2\text{N}^+\text{H}^\cdot\text{MY}^- + \text{X}^- \]  \hspace{1cm} (2)

Thus the amine salt, and not the free amine, should be considered as being the extracting agent.
In the acid sulfate systems, the importance of pH becomes more pronounced than in the nitrate or chloride systems due to the dibasic character of sulfuric acid, a character which gives it the ability of forming sulfate-bisulfate equilibrium, i.e.,

\[
\begin{align*}
H_2SO_4 & = H^+ + HSO_4^- \quad (3) \\
HSO_4^- & = H^+ + SO_4^{2-} \quad (4)
\end{align*}
\]

The aqueous speciation distribution of uranium was calculated in the sulfate leach slurry and represented in Fig. 8. The results showed that the complexes of \( UO_2SO_4 \), \( UO_2(SO_4)_2^{2-} \) were the predominant species in the pH range 0 – 6. At near neutral and alkaline pH conditions, \( U^+ \)-hydroxide complexes start to dominate the aqueous phase. At pH 7, the \( UO_2(OH)_2 \cdot H_2O\text{(C)} \) became the main species. At pH 12, \( UO_2(OH)_3 \) became the predominant species. The formation of \( UO_2(OH)_2 \cdot H_2O\text{(C)} \) species started to grow after pH 10.

![Fig. (8): Predicted aqueous speciation of U(VI) by Hydra-MEDUSA, a chemical equilibrium calculation program](image)

At the working leach slurry pH (1.1), the expected uranium species are \( UO_2SO_4 \) and \( UO_2SO_4 \). Accordingly the predictable extraction mechanisms of uranium by use Tri-butyl amine (TBA) were anionic or neutral as follows: \(^{18-20}\),

\[
\begin{align*}
(R_3NH)_2SO_4 + UO_2(SO_4)_2^{2-} & = (R_3NH)_2UO_2(SO_4)_2 + SO_4^{2-} \quad (5) \\
or & \\
(R_3NH)_2SO_4 + UO_2SO_4 & = (R_3NH)_2UO_2(SO_4)_2 \quad (6)
\end{align*}
\]

4. Uranium Stripping

Uranium stripping from the working solvent (TBA) which was obtained by applying the above mentioned conditions and an assay of 0.978 gU/l. The effects of the following factors, namely, stripping agent, concentration of the stripping agent, shaking time and organic/aqueous phase ratios were investigated.

4.1. Effect of Stripping Agent

The following stripping agents, namely; \( H_2SO_4 \), \( Na_2CO_3 \), HCl, HNO\(_3\) and \( H_2O \) were studied. The latter mentioned stripping agents (1 M each) was shooked with the working solvent with aqueous/organic phase ratio of 2/1 for 30 min. shaking time. From the obtained results plotted in Fig. (9) it was found that, sulfuric acid could be choiced as a suitable stripping agent.
4.2. Effect of Stripping Agent Concentration

To study the effect of stripping agent concentration, a series of stripping experiments were performed by shaking different concentrations of sulfuric acid ranging from 1 up to 9 M, with the working solvent, at an aqueous/organic phase ratio of 2/1, for 30 min. shaking time. From the obtained results (Fig. 9), it is obvious that stripping efficiency increases from about 47 to 96% at a sulfuric acid concentration of 1 to 9 M sulfuric acid respectively. In other words, a relatively strong sulfuric acid is quite sufficient to strip more than 96% of the loaded uranium.

4.3. Effect of Shaking Time upon Uranium Stripping Efficiency

For studying the effect of shaking time on uranium stripping from the uranium-working solvent, a series of stripping experiments were performed using time intervals varying from 5 up to 60 minutes. The performed experiments were carried out using a fixed sulfuric acid concentration of 9 M and 2/1 A/O ratio. The obtained results indicate that 30 minutes contact time would be quite sufficient for stripping about 96% of uranium from the working solvent (Fig. 10).
Fig (10): Effect of shaking time upon uranium stripping from the loaded solvent (stripping agents type H$_2$SO$_4$, stripping agents conc. 9M aqueous/organic phase ratio of 2/1)

4.4. Effect of O/A Phase Ratio upon Uranium Stripping Efficiency, and Construction of McCabe Thiele Stripping Diagram

In order to study the effect of the phase ratio on uranium stripping efficiency from the uranium-loaded TBA a sample was prepared by SIP extraction of uranium from Gattar granite GII diluted leaching slurry and a series of stripping experiments were performed using O/A ratios ranging from 4/1 down to 1/4. In these experiments, the other stripping conditions were fixed at 9 M sulfuric acid for 30 min shaking time. The obtained data (Table 1) were used to construct the equilibrium isotherm in the McCabe Thiele diagram (21, 22) (Fig.11). The latter was used to calculate the theoretical stages required for almost complete uranium stripping from the uranium-loaded solvent sample of Gattar granite GII diluted leaching slurry. From the constructed diagram, it is obvious that an almost three theoretical stages are required for the removal of almost all uranium from the working solvent sample obtained from sample of Gattar granite GII diluted leaching slurry at the operating line slope of 1.

Table (1): Effect of O/A phase ratio upon uranium stripping efficiency from the uranium loaded solvent of Gattar granite GII diluted slurry sample

<table>
<thead>
<tr>
<th>O/A Ratio</th>
<th>U Conc., mg/l</th>
<th>S°</th>
<th>Stripping eff., %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Org.</td>
<td>Aq.</td>
<td></td>
</tr>
<tr>
<td>4/1</td>
<td>788</td>
<td>760</td>
<td>0.96</td>
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<tr>
<td>3/1</td>
<td>731</td>
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<td>2/1</td>
<td>618</td>
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<td>313.5</td>
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</tr>
<tr>
<td>1/4</td>
<td>10.7</td>
<td>241.8</td>
<td>22.59</td>
</tr>
</tbody>
</table>
CONCLUSION

Considering the preferred conditions for extraction of uranium from Gattar granite GII leaching slurry by applying solvent-in-pulp (SIP) deduced from the present work, about 91% of uranium could be extracted using a solvent (TBA) concentration of 20% in kerosene, extraction time of 60 min., solid content of 102 g/l, using glue as non-ionic hydrophilic surfactant with concentration of 100 g/l and slurry/organic phase ratio of 4/1. About 96% of the loaded uranium on the working solvent could be stripped using 9 M sulfuric acid as an effective striping agent at an aqueous/organic phase ratio of 4/1 for 30 min. contact time. Based on the stripping results the McCabe-Thiele, uranium stripping diagram was drawn and most of the loaded uranium could be stripped after three stripping theoretical stages.

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