A REVIEW OF URANIUM SOLVENT EXTRACTION: ITS PRESENT STATUS AND FUTURE TRENDS

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Abstract

In this paper, the present status and future trends of uranium solvent extraction has been reviewed by focusing on the AMEX process. Some problems commonly encountered in current industrial operations were reviewed including crud formation caused by soluble silica, tertiary amine degradation by oxidation, recovery of vanadium and molybdenum, thorium treatment and operation difficulties with high chloride concentrations. Possible solutions were described and commented in terms of industrial practice. Future research trends of uranium solvent extraction have been suggested.

1. Introduction

Yellow cake is the preliminary marketable uranium product as nuclear fuel material. Many processes have been developed and operated to produce yellow cake from various types of ores. Key factors of the processes were described by Lunt et al. (2007). Generally, the process options for treating various types of uranium ores follow the four routes as shown in Fig. 1.

Fig. 1: Process options for treating various types of uranium ores (Based on Anon. 1993).

Detailed conditions for uranium leach, purification and precipitation to produce yellow cake in various uranium hydrometallurgical processes were reviewed
by Edwards and Oliver (2000) and Ivanova et al. (2009). These reviews show
that solvent extraction (SX) and ion exchange (IX) play key roles in uranium
purification from leach solutions. Although either SX or IX could be selected
depending on the specific flowsheet (Tonder and Kotze 2007), normally when
the uranium concentration in acid leach solution is high, for example, >800-
900 mg/L U, SX is more preferable than IX in term of costs (Tonder and Kotze
2007, Ivanova et al. 2009). Additionally, solvent extraction is also widely used
and investigated for uranium recovery as a by-product from processes for
manufacturing phosphoric acid (Waters et al. 2008) and treating rare earth
ores (Taylor 2007). Many commercialised SX processes were described
extensively by Ritcey (2006). The DAPEX process with D2EHPA (Di-2-
ethylhexylphosphoric acid) as the extractant is the first developed and
commercialised SX process to recover uranium from sulphuric acid leach
solutions. However the DAPEX process was superseded by the AMEX
process with amines as the extractant because tertiary amine is more
selective for uranium extraction than D2EHPA in sulphuric acid leach
solutions. Although tertiary amines have been widely accepted in industrial
practices, problems still exist in some applications, particularly with new
uranium resources and associated resources to recover uranium as a by-
product. Some investigations were conducted recently to meet specific
requirements.

Up to now, no satisfactory solvent extraction process has been found to
recover uranium from carbonate leach solutions commercially. Although some
meaningful investigations were conducted on the application of SX for
recovering uranium from alkaline solutions (Clifford et al. 1957), it is still a
significant challenge to develop an effective SX process to recover uranium
from alkaline solutions.

In this paper, common problems encountered in the widely used AMEX
process were highlighted and recently developed methods to solve these
problems were discussed. Some new investigations for special cases of
uranium SX are also summarised in the current paper.

2. **U(VI) solvent extraction with amine**

Tertiary amine is the main extractant for the AMEX process. Uranium SX
using tertiary amines was summarised and reviewed by Mackenzie (1997),
Ritcey (2006), Ivanova et al. (2009) and Crane et al. (2010). Uranium
extraction reactions with tertiary amines are reported by a number of authors
with some differences (Coleman 1958, Yakubu and Dudeney 1987,
Mackenzie 1997, Ivanova et al. 2009). Among these reported expressions,
most possible reactions are suggested as follows (with a top bar to donate
organic species).

\[
2R_3N + H_2SO_4 = (R_3NH)_2SO_4 \quad (1)
\]

\[
2(R_3NH)_2SO_4 + UO_2(SO_4)^{4-} = (R_3NH)_4UO_2(SO_4)_3 + 2SO_4^{2-} \quad (2)
\]
Among these reactions, Equation 1 is the acidification step. The distribution of sulphuric acid between the organic (Alamine 336) and aqueous phases varied with pH values and demonstrated “Λ” shapes with different Alamine 336 concentrations as shown in Fig. 2 (Yakubu and Dudeney 1987). This indicates that the acidification of tertiary amines could reach a maximum value called “saturation” of acidification (Yakubu and Dudeney 1987).

Fig. 2: Distribution of H$_2$SO$_4$ under various equilibrium pH values with different concentrations of Alamine 336 in kerosene (Based on Yakubu and Dudeney 1987).

Equations 2 and 3 describe the extraction of uranium by anionic exchange. From these equations, it is known that the acidity does not affect the uranium extraction directly. However, the acidification degree of amine is affected by the aqueous solution acidity. Therefore, the uranium extraction is affected by the aqueous solution acidity indirectly. With Alamine 336 as the extractant, the uranium extraction decreased with the increase in the pH value when the pH was higher than 1 as shown in Fig. 3 (Yakubu and Dudeney 1987). This is caused by the insufficient acidification of amine with the increasing pH. However, when the acidity was increased to a certain value and the acidification of amine reached saturation, further increase in the acidity decreased the uranium extraction as shown in Fig. 4 (Mackenzie 1997) due to the competition extraction of H$_2$SO$_4$ with elevated acid concentrations.
Fig. 3: Distribution of U(VI) (1.8 g/L) under various equilibrium pH values with different concentrations of Alamine 336 in kerosene (Based on Yakubu and Dudeney 1987).

Fig. 4: Uranium extraction distribution isotherms with different H₂SO₄ concentrations (based on Mackenzie 1997)
The increase in the \( \text{SO}_4^{2-} \) concentration is favourable to form extractable uranium species of \( \text{UO}_2(\text{SO}_4)_2^{3+} \) and \( \text{UO}_2(\text{SO}_4)_2^{4+} \) in the aqueous phase. However it is unfavourable to the extraction of \( \text{UO}_2(\text{SO}_4)_2^{4+} \) and \( \text{UO}_2(\text{SO}_4)_2^{2+} \) with the acidified amine because \( \text{SO}_4^{2-} \) can prohibit their extraction according to Equations 2 and 3. Slight excess of \( \text{SO}_4^{2-} \) is required for maximum uranyl sulphate extraction as shown in Fig. 5 (Coleman et al. 1958).

![Fig. 5: Effect of sulphate concentration on U(VI) extraction with tri-n-octyl amine (TOA) (based on Coleman et al. 1958).](image)

Most impurities present in the uranium leach solution are not extractable with tertiary amine as they do not form or form very weak anionic complexes with \( \text{SO}_4^{2-} \). These impurities include Fe(III), Al(III), RE(III), V(V) and divalent metal ions etc. The selectivity of tri-isooctylamine (TIOA) for different ions was reported by Coleman et al. (1958) as shown in Table 1.
Table 1: Selectivity of tri-iso-octylamine for different ions (1 M $\text{SO}_4^{2-}$, pH=1, ~1 g/L metal ions, A/O=1:1, 0.1 M amine in hydrocarbon diluents) (based on Coleman et al. 1958)

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Extraction distribution coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>U(VI)</td>
<td>90</td>
</tr>
<tr>
<td>V(IV), Ti(IV), Ce(IV), Fe(III), Al(III), RE(III), Cr(III), Fe(II), Co(II), Ni(II), Mn(II), Cu(II), Zn, Ca, Mg.</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>V(V)</td>
<td>&lt;1; ~20 (5g/L V, pH=2)</td>
</tr>
<tr>
<td>Mo(VI)</td>
<td>150 (3g/L Mo); &gt;1000 (3g/L Mo, pH=2)</td>
</tr>
<tr>
<td>Zr(IV)</td>
<td>10-200 (Moore 1960)</td>
</tr>
<tr>
<td>Th(IV)</td>
<td>&lt;0.1 (0.5M $\text{SO}_4^{2-}$)</td>
</tr>
</tbody>
</table>

Obviously, co-extracted metals with U(VI) by tertiary amine are Mo(VI), Zr(IV) and V(V) especially at higher pH such as 2. Mo(VI) extraction with tertiary amine is stronger than that of U(VI) within the extraction pH range of 0.5-2 as shown in Fig. 6. For vanadium, only V(V) can be extracted by tertiary amine at a relatively high pH such as 2. Therefore, if vanadium is present in the feed solution, its co-extraction can be controlled by reducing V(V) to V(IV) using iron powder (Crane et al. 2010). In sulphuric acid solution zirconium forms $\text{Zr(SO}_4)_4^{3-}$ complex and can be extracted with tertiary amine in the form of $\text{R}_3\text{NH}_4\text{Zr(SO}_4)_4$. The extraction efficiency increases with the increase in the length of the alkyl group of the tertiary amine and decreases when the alkyl group is branched (Sato and Watanabe 1974). Zirconium extraction can be suppressed by the addition of phosphate (Anon. 1993). Normally, zirconium was removed by adjusting the pH to around 2.8 with ammonium sulphate solution in the scrubbing stages (Ivanova 2009, Crane et al. 2010). Some anion ions can also be extracted by tertiary amine, causing the decrease in the amine loading capacity for uranium. The extraction order is reported to be $\text{UO}_2(\text{SO}_4)_4^{3+} > \text{NO}_3^- > \text{Cl}^- > \text{HSO}_4^- > \text{F}^-$ (Coleman 1958, Mackenzie 1997). Chloride as an impurity anion commonly exists in the uranium leach solution derived from the ore minerals, the ore moisture, the site make-up water and/or sodium chlorate. Uranium loading with Alamine 336 under different concentrations of chloride in the feed solution was investigated by Soldenhoff et al. (2000) and is shown in Fig. 7. It is evident that as the concentration of the chloride increases, the loading of uranium in the Alamine 336 was reduced significantly. When the chloride concentration increased to 8 g/L, the loaded uranium concentration in the organic solution reduced to half compared with no chloride presence in the feed solution (Fig. 7).
Fig. 6: Extraction of U(VI) and Mo(VI) with 0.1 M Alamine 336 and 5% isodecanol in kerosene from sulphate solution (based on Ritcey 2006). Metal concentration in feed (g/L): 1.00 U, 1.01 Mo; A/O=3:1.

Fig. 7: Uranium extraction distribution isotherms with Alamine 336 for different chloride concentrations in the feed solutions (based on Soldenhoff et al 2000). Organic solution: 5% (v/v) Alamine 336 and 2% (v/v) isodecanol in Shellsol D70; Aqueous solution: 1.6 g/L U; Equilibrium pH: 1.5.
3. Application of tertiary amine in the AMEX process

The AMEX process was developed by the use of solvent extraction with amine, usually tertiary amine, as the extractant to recover uranium from acidic sulphate solutions (Coleman et al. 1958). For the acidic leach solutions containing low uranium concentration from low grade uranium ores, Eluex (IX+SX), Bufflex (IX+SX) and Purlex (direct SX) processes were developed (Ritcey 2006). In these processes, the SX steps are very similar. The main differences of these processes are found in scrubbing and in the production of final uranium products.

The conceptual flowsheet to recover uranium is shown in Fig. 8. In industrial practice, Alamine 336 (a tri-octyl/decyl amine) is popularly selected as the extractant. Similar product of Adogen 364 (a tri-octyl/decyl amine) is also used in some cases. The difference between them is the ratio of trioctyl amine and tridecyl amine. If the leach solution contains vanadium or molybdenum, amines with higher molecular weight should be considered to increase the miscibility of the metal-amine complexes with the diluent to avoid the formation of third phases (Ivanova et al. 2009). For example, trilaurylamine can be used when molybdenum is present because the molybdate-C$_{12}$ amine complex formed is much more organic soluble than the molybdate-C$_{8}$ amine complex (Mackenzie 1997).

Fig. 8: A conceptual flowsheet of the AMEX process for uranium recovery from acidic leach solutions. ADU: ammonium diuranate; SDU: sodium diuranate.

Alkyl alcohols are effective additives to eliminate third phase occurrence. Isodecanol with 2-5% (v/v) concentration is commonly used as the modifier for uranium extraction with Alamine 336. The presence of an alcohol additive could increase the uranium extraction to some extent with amines (Coleman
Uranium extraction with Alamine 336 is usually operated under pH around 1.5 to ensure the maximum uranium loading. The theoretical maximum loading of uranium with Alamine 336 is about 1.2 g/L U in per 1% (v/v) solvent (Mackenzie 1997, Crane et al. 2010). In practice, 75-80% maximum loading capacity or about 1 g/L U loading per 1% (v/v) Alamine 336 is often used as the basis for the process design (Crane et al. 2010). Normally 3-5% (v/v) Alamine 336 in a diluent is considered for uranium extraction (Ritcey 2006).

Because of the high selectivity of U(VI) extraction with tertiary amine over other impurities, scrubbing is very simple to generate uranium solutions with desired purity. A number of processes only have one washing stage with water to remove entrained or adsorbed impurities such as iron, arsenic, calcium, magnesium etc. Some processes are operated without scrubbing stages. Few processes have 3 or 4 scrubbing stages with acidified water and ammonium hydroxide to remove impurities. If molybdenum or zirconium is present in the solution, they will be built up in the organic solution. Sodium carbonate solution is used to remove them from the bleeding barren organic solutions to maintain balance (Ritcey 2006).

A number of reagents can be applied to strip uranium from loaded amine solvent such as nitrates, chlorides, sulphates, carbonates, hydroxides and acids. Most frequently used reagents are ammonium sulphate and sodium chloride due to their advantages of simple operation, desired product and/or economical effectiveness (Ritcey 2006, Taylor 2007, Connelly 2008). A comparison of uranium stripping with ammonium sulphate and sodium chloride is shown in Table 2.

The recirculation of chloride can result in its built-up in the solvent and lead to reduction of its loading capacity. Investigations were carried out intending to replace chloride stripping with ammonium sulphate or sulphuric acid stripping (Morais and Gomiero 2005, Morais et al. 2005). One current trend, in Canada in particular, is stripping with strong sulphuric acid followed by precipitation of uranium peroxide with hydrogen peroxide to avoid ammonia release concern (Taylor 2007). Sodium carbonate is also used in some operation mills (Ritcey 2006). However no obvious advantage was observed by strong sulphuric acid stripping to replace chloride, therefore it is not widely accepted in the industry.
Table 2: Comparison of uranium stripping with ammonium sulphate and sodium chloride

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Optimum operation</th>
<th>Advantage</th>
<th>Disadvantage</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH₄)₂SO₄</td>
<td>• (NH₄)₂SO₄ : ~1.0 M (120-150 g/L);</td>
<td>• No impurity metal introducing;</td>
<td>• Not suitable to the solution containing Mo;</td>
<td>Mackenzie 1997;</td>
</tr>
<tr>
<td></td>
<td>• pH: 3.5-5 (adjusted with ammonia);</td>
<td>• Producing ADU with ammonia precipitation;</td>
<td>• Ammonium release to the environment.</td>
<td>Ritcey 2006;</td>
</tr>
<tr>
<td></td>
<td>• stage number: 4</td>
<td>• High purity product (97-98 % U₃O₈).</td>
<td></td>
<td>Morais and Gomiero 2005;</td>
</tr>
<tr>
<td></td>
<td>• U₃O₈ in strip liquor: ~20-30 g/L</td>
<td></td>
<td></td>
<td>Vanova 2009;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Crane et al. 2010.</td>
</tr>
<tr>
<td>NaCl</td>
<td>• NaCl: ~1.0-1.5M;</td>
<td>• Reagent cost effectiveness;</td>
<td>• Possible Cl built-up in solvent due to the barren NaCl solution recirculating;</td>
<td>Boydell, 1980;</td>
</tr>
<tr>
<td></td>
<td>• pH: 2~3;</td>
<td>• Selective stripping of U(VI) over Mo(VI);</td>
<td>• Product containing sodium with low purity (85~88% U₃O₈).</td>
<td>Morais et al. 2005;</td>
</tr>
<tr>
<td></td>
<td>• stage number: 4;</td>
<td>• Precipitation with cheap base such as MgO, CaO.</td>
<td></td>
<td>Ritcey 2006;</td>
</tr>
<tr>
<td></td>
<td>• U₃O₈ in strip liquor: ~30-40 g/L</td>
<td></td>
<td></td>
<td>Connelly 2008;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ivanova 2009.</td>
</tr>
</tbody>
</table>

4. **Challenge of uranium extraction with tertiary amine**

Uranium solvent extraction with tertiary amine has been successfully operated worldwide in a large number of process mills for a long period of time. Some problems still exist in process operations particularly in new process development and operations (Mackenzie 1997, Ivanova 2009, Crane et al. 2010).

4.1. **Crud formation by dissolved silica**

Crud formation is a common problem in solvent extraction processes and could result in difficult process operation and lead to high solvent loss. Many factors can cause crud formation such as the composition of the feed solution, the nature of the solvent, organic degradation, equipment selection and method of operating etc. Methods have been developed and the crud formation was successfully solved in some specific processes (Ritcey 1980, Jaaskelainen et al. 1998). Importantly, considerable attention should be paid to the crud formation caused by the soluble silica which contains in most uranium acidic leach solutions, particularly, the one with agitated leach operation. Typical soluble silica concentration is in the range of 300-700 ppm, but in some cases, it could reach as high as 5000 ppm (Mackenzie 1997). Soluble silica exists in acidic leach solutions in the form of Si(OH)₄. It can polymerise slowly in acidic solutions and more rapidly when the pH increases (Ivanova et al. 2009). The possible mechanism of crud formation caused by soluble silica and trouble-shooting methods are shown in Table 3.
Table 3 Crud formation mechanism by soluble silica and trouble-shooting in uranium solvent extraction with tertiary amine

<table>
<thead>
<tr>
<th>Possible mechanism of crud formation</th>
<th>Trouble –shooting method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Si(OH)_4 polymerisation gradually to form solid particles.</td>
<td>• Ore blending to resolve the problem;</td>
<td>Ritcey 1980</td>
</tr>
<tr>
<td>• Si(OH)_4 and its polymer adsorbed on the interface by amine, isodecanol modifier or polyacrylamide flocculant.</td>
<td>• Organic continuous operation to prohibit the coalescence of adsorbed solids due to their aqueous wetting property;</td>
<td>Mackenzie 1997, Ivanova et al. 2009, Crane et al. 2010.</td>
</tr>
<tr>
<td></td>
<td>• Appropriate usage of flocculant.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Addition of certain surfactants to lower surface tension and reduce surface adsorption</td>
<td></td>
</tr>
</tbody>
</table>

4.2. Tertiary amine degradation

Serious degradation of tertiary amine caused by nitrate (Munyungano 2007, Feater et al. 2009, Rensburg and Munyungano 2009) and by the presence of V(V) (Chagnes et al. 2008, 2010, 2011) has been reported. Although this problem does not happen widely in the uranium industry, sufficient attention should be paid if the feed solution contains nitrate or high concentration of vanadium. Fortunately, leaching economical uranium ore body with sulphuric acid does not generate nitrate (Edwards and Oliver 2000). Nitrate in the Rossing uranium process is reported from the mining explosives entrancing to the process water in the open pit (Rensburg and Munyungano 2009) and from nitrate leaching for the Bufflex project (Feater et al. 2009). Based on the gas chromatography analysis, identified degradation products of Alamine 336 by nitrate oxidation are secondary amine, nitrosoamine (R2N-NO) and alkyl aldehydes. Possible mechanism was suggested by Feather at el. (2009). The degradation can be catalysed by the presence of molybdenum (Munyungano 2007). Effective measures to control this degradation are:

- Keeping redox potential lower than 500 mV in the feed solution and extraction stages;
- Maintaining Fe^{2+}/Fe^{3+} ratio higher than 1:2.5;
- Keeping nitrate concentration less than 250 mg/L in stripped solvent and less than 2500 mg/L in ammonium sulphate strip solution.

Vanadium is widely associated with uranium ores. Usually, vanadium exists in the uranium acidic leach solutions almost all as V(IV) under redox potential lower than 600 mV (Crane et al., 2010). V(IV) can not be extracted by tertiary amine therefore it can be rejected to the raffinate effectively in the amine process. However, if vanadium concentration is high, for example higher than 200 mg/L in the pregnant leach solution, and no good measure is taken to control the solution Eh in a proper range, V(IV) could be oxidised to V(V) which can be readily extracted by the amine and cause its degradation. The main degradation product of Alamine 336 is secondary amine (Chagnes et al. 2008). In addition, unsaturated tertiary amine and N,N-diaklkyl formamide are
also been identified (Crane et al. 2010). Mechanism of tertiary amine degradation caused by V(V) is complicated and possible chemical routes are supposed inconsistently by Crane et al. (2010) and by Chagnes et al. (2011). A large amount of secondary amine present in the solvent can lower the loading capacity and insufficient separation due to the stronger co-extraction of impurities. V(V) can be rapidly reduced to V(IV) by ferrous ions. More effective measure is to strictly control the Eh in the feed solution to below 500 mV by adjusting the Fe^{2+}/Fe^{3+} ratio. Some uranium plants use iron wire set in the equipment during the solvent extraction process to ensure vanadium maintaining in V(IV) (Ritcey 2006). A number of suggestions were raised by Chagnes et al. (2008) to avoid or delay the degradation of tertiary amine:

- The use of more stable modifier such as alkyl alcohols was supposed to substitute isodecanol which is readily decomposed by V(V), resulting in the acceleration of the degradation of tertiary amines;
- The replacement of aliphatic kerosene by aromatic kerosene;
- The use of anti-oxidant agent in the SX system;
- The use of more stable extractant to substitute tertiary amines.

### 4.3. Molybdenum and vanadium recovery

Molybdenum and vanadium are often present in uranium acidic leach solutions. If molybdenum present, uranium selective stripping should be conducted with acidic chloride, leaving molybdenum in the organic phase. Subsequently molybdenum was stripped with carbonate (McDonaldt et al. 1981, Ritcey 2006). Ammonium sulphate or sulphuric acid are unsuitable for uranium stripping due to their poor selectivity of uranium over molybdenum. As Mo(VI) extraction is stronger than U(VI) with tertiary amine, the presence of Mo(VI) will decrease the uranium extraction or the loading capacity of the amine. Furthermore, the solubility of the complex of Mo(VI) with tertiary amine is low in aliphatic diluents. As a result, third phase and green-yellow crud could form (McDonaldt et al. 1981, Moyer and McDowell 1983). The allowable maximum molybdenum concentration in the solution is about 400-500 mg/L using 5% (v/v) Alamine 336 as the extractant and with 3% (v/v) isodecanol as the modifier in the Napoleum diluent (McDonaldt et al. 1981). Heavier molecular and more branched tertiary amines, such as Alamine 304 (tri-lauryl amine), are suggested to increase the solubility of the complex of molybdenum with the tertiary amine (McDonaldt et al. 1981, Moyer and McDowell 1983). A new reagent called IX-8A was developed to selectively extract molybdenum from uranium sulphate solution. However, it is not commercially available (McDonaldt et al. 1981). Mohanty et al. (1991) studied the extraction of Mo(VI) and U(VI) with LIX 622 (a mixture of 5-dodecylsalicylaldoxime and tri-decanol) and discovered that LIX 622 can extract Mo(VI) under a very strong acid condition while the extraction of U(VI) starts from pH 3. With LIX 622 as the extractant, Mo(VI) can be readily separated from uranium before its extraction with amine. Edmond et al. (1992) A patented method to separate molybdenum from uranium with chelating hydroxime reagents, such as LIX 63 (an aliphatic hydroxyoxime). High extraction selectivity of molybdenum over uranium could be obtained below
pH 3.0 and when substantial molybdenum was extracted, almost no uranium was extracted with LIX 63.

At present, vanadium is recovered in a separate SX circuit from the raffinate of uranium extraction with the same tertiary amine as the extractant. After uranium extraction, the raffinate Eh was elevated to above 680 mV and all vanadium could be converted to V(V) (McDonald et al. 1981). Hydrogen peroxide is normally used as the oxidant (Ivanova 2009). Under such high redox potential, tertiary amine is degraded to its corresponding secondary or primary amine. In fact, a large amount of secondary amine and other degradation products in vanadium SX circuits were identified (Crane et al. 2010). Fortunately, these degradation products do not impact vanadium extraction and in contrary, secondary and primary amines can enhance vanadium extraction.

4.4. Thorium treatment

Thorium is an impurity element for uranium product. Although it can be readily rejected to the raffinate in uranium solvent extraction with tertiary amine due to its low extraction, it can build up to an unacceptable level when the raffinate solution is recycled. Thorium must be removed to ensure the uranium product quality. Although thorium could be a potential nuclear fuel in the future, it has no or limited market currently. Thorium (mainly Th-232) is a radioactive element and could cause environmental concern if it is disposed improperly. It should be considered to convert it into stable compounds for storing in tailing dams or for land fill (Crane et al. 2010).

The recovery of thorium from acidic sulphate solutions using primary amine was investigated extensively (Crouse and Brown 1959, Borrowman and Rpsenbaum 1962, Yamani and Shabana 1985). When monazite is processed with acid leaching to recover rare earths and uranium, a considerable amount of thorium enters the leach solution. It is suggested that thorium is recovered for storing as a potential future nuclear resource. Primary amine can be used to selectively extract thorium over rare earths and uranium meanwhile tertiary amine can be used to selectively extract uranium over rare earths and thorium from sulphuric acid leach solutions as shown in Figs. 9 and 10. The mixture of primary and tertiary amines can be used to separate both thorium and uranium from rare earths simultaneously (Amaral and Morais 2010).
Fig. 9: Effect of concentration of Primene JM-T (a primary amine) on metal extraction (based on Amaral and Morais 2010). Composition of the aqueous solution (g/L): RE₂O₃ - 36.2, ThO₂ -3.25, U₃O₈ - 0.17, SO₄²⁻ - 94, P₂O₅ – 15.1; Phase ratio: 1.1; Temperature: ~25 °C.

Fig. 10: Effect of concentration of Alamine 336 (a tertiary amine) on metal extraction (based on Amaral and Morais 2010). Composition of the aqueous solution (g/L): RE₂O₃ - 36.2, ThO₂ -3.25, U₃O₈ - 0.17, SO₄²⁻ - 94, P₂O₅ – 15.1; Phase ratio: 1.1; Temperature: ~25 °C.

4.5. Solutions with high chloride concentrations

Chloride exists in most uranium sulphuric acid leach solutions. Normally its concentration is less than a bearable level like 2 – 3 g/L for uranium recovery with tertiary amine. However in some regions the processing water available for uranium ore treatment contains appreciable chloride. This particularly
occurs in South and West Australia and in Namibia where low chloride water is extremely short (Ivanova 2009). The use of desalination to obtain process water would largely increase operating costs. In Olympic Dam, Beverly and Honeymoon of South Australia, the uranium SX process using tertiary amine is adversely affected by the process water containing 3-8 g/L Cl (Brooy et al. 2009). When large amount of chloride presents in the solution, not only uranium loading is reduced significantly due to the competing extraction, but also the selectivity for uranium over Fe(III) is reduced due to the extraction of FeCl₄⁻. Traditional tertiary amine process is not suitable for the solution with high chloride concentration in terms of operating costs. A new process with a mixture of D2EHPA and tertiary amine was developed for such a solution with high chloride concentration in Honeymoon (Soldenhoff et al. 2000 and 2005, Brooy et al. 2009). For an aqueous feed solution containing 9.5 g/L Cl, with an organic system containing 6% (v/v) Alamine 336 and 4% (v/v) iso-decanol the extraction distribution coefficient of uranium was only 1.6. With an organic system containing 1% (v/v) D2EHPA and 2.5% (v/v) Alamine 336, it reached 1094. This indicates that uranium extraction with D2EHPA is much stronger than that with Alamine 336 when high chloride presented in the feed solution.

When amine was added into the D2EHPA solvent, uranium loading could be decreased. For example, with 4% (v/v) D2EHPA, uranium maximum loading is 6.8 g and when 5% (v/v) amine was added the uranium maximum loading reduced to 5.8 g (Brooy et al. 2009). Amine plays a significant role to suppress Fe(III) extraction with D2EHPA. As shown in Fig. 11, the extraction of Fe(III) with D2EHPA decreased significantly with the addition of amine. Secondary amine and tertiary amine are more effective than primary amine to lower Fe(III) extraction.

![Fig. 11: The effect of pH and the composition of the organic system on the extraction of ferric ions (based on Soldenhoff et al. 2000). Organic concentration: 5% (v/v) in Shellsol D70; Fe(III): 10 mg/L; Cl⁻: 8 g/L, A/O=1:1, room temperature.](image)

Fig. 11: The effect of pH and the composition of the organic system on the extraction of ferric ions (based on Soldenhoff et al. 2000). Organic concentration: 5% (v/v) in Shellsol D70; Fe(III): 10 mg/L; Cl⁻: 8 g/L, A/O=1:1, room temperature.
A considerable amount of impurities such as Fe(III), Ti(IV), V(IV) was co-extracted with uranium(VI) due to the poor selectivity of D2EHPA. The co-extraction of these metals can be suppressed to some extent with the addition of amine into D2EHPA. Most of impurities could be removed by scrubbing with sulphuric acid. However, some could remain in the organic solution and advanced to the stripping stages. When uranium was stripped with sodium carbonate, gelatinous precipitation could occur with the impurities, causing the formation of cruds or phase separation difficulties (Soldenhoff et al. 2000, Brooy et al. 2009).

There are two obvious drawbacks with the system containing both D2EHPA and amines compared with traditional DAPEX SX system. One is the decrease in the uranium maximum loading with the addition of amines. The other is the consumption of acid in the extraction stages for acidification of the amine (Equation 11 and 4) and the consumption of base in the stripping stages (Equations 5-6).

\[
R_3NH + HCl = R_3NCl \tag{4}
\]

\[
(R_3NH)_2SO_4 + 2Na_2CO_3 = 2R_3N + Na_2SO_4 + 2NaHCO_3 \tag{5}
\]

\[
R_3NCl + Na_2CO_3 = R_3N + NaCl + NaHCO_3 \tag{6}
\]

Mini pilot plant tests and large scale demonstration plant tests were carried out for processing acid leach solutions of Honeymoon uranium ore using underground water containing about 8 g/L Cl (Soldenhoff et al. 2005, Brooy et al. 2009). Reasonably good results with more than 98% uranium recovery were obtained. No commercial plant has been reported in operation with this process. At present for processing uranium acid leach solution, the presence of chloride in high concentration is still a challenge in terms of operation costs.

5. U(VI) extraction from carbonate leach solutions

Comparatively, alkaline leach with carbonate and bicarbonate is much more selective than acidic leach. Only molybdenum and vanadium, if present, in the ore could be troublesome for the uranium purification. Normally, molybdenum dose not co-precipitated with uranium and can be removed by bleeding after the uranium precipitation (Preez 1989). Several methods were used to remove vanadium for uranium purification (Preez 1989, Lunt et al. 2007). In commercial carbonate leach operations, it is common to remove vanadium by the addition of lead sulphate or ferrous sulphate in the PLS to form lead or ferrous vanadates precipitates selectively before uranium precipitation. When ion exchange resin was used, vanadium could be separated from uranium by elevated pH above 10 in the feed solution. However, uranium adsorption would be reduced significantly (Preez 1989, Lunt et al. 2007).

Solvent extraction method should have some advantages in regards to its flexibility of uranium concentration in the PLS and possible selectivity over
vanadium and molybdenum. However currently, no solvent extraction technology has been reported for uranium recovery from carbonate leach solutions. Instead, ion exchange with strong base resin and/or direct precipitation is the preferred method (Edwards and Oliver 2000). To develop a suitable SX system to extract uranium selectively in carbonate solutions is a significant challenge.

Uranium carbonate complex species in the leach solution is reported to be \( \text{UO}_2(\text{CO}_3)_3^{4-} \). Normal extractants are ineffective to extract this species. A large number of investigations carried out in 1950’s showed that some complexing agents such as benzoin 2-oxime, cupferron, hydroxylamine, pyrogallol and 8-quinolinol gave substantial uranium extraction (Clifford et al. 1957). 8-quinolinol and Arquad 2C, \((\text{R}_2\text{N(CH}_3)_2\text{Cl})\) showed synergistic extraction of uranium in a carbonate solution. The extraction reaction was expressed as (Clifford et al. 1957):

\[
\overline{\text{R}}_4\text{NCl} + 3\text{HOx} + \text{UO}_2(\text{CO}_3)_3^{4-} = \overline{\text{R}}_4\text{NUO}_2(\text{Ox})_3^- + 3\text{HCO}_3^- + \text{Cl}^{-}
\]  

where \( \text{HOx} \) donates one of the extractants mentioned above. NaCl could be applied as the stripping agent for this organic system. There is no further investigation in this area in recent years. In order to apply solvent extraction to uranium recovery from carbonate leach solutions, effective and economical organic systems should be developed.

**Summary**

Historically, the DAPEX process using D2EHPA was first developed to recover uranium from its acid leach solutions. In recent years, the DAPEX process has been replaced by the AMEX process with tertiary amine as the extractant due to its far better selectivity for uranium over impurities than that of D2EHPA. However, some problems could be encountered with the traditional AMEX process, particularly in the aspects of:

- Crud formation from soluble silica;
- Tertiary amine degradation by oxidation;
- Vanadium and molybdenum removal and recovery;
- Thorium treatment; and
- Process improvement with the presence of chloride.

To solve these problems, future research and development in uranium solvent extraction are suggested to focus on:

- Developing new active interfacial modifier to eliminate or alleviate crud formation caused by soluble silica;
- Developing solvent extraction processes to recover vanadium and molybdenum before uranium recovery;
- Evaluating the use of primary amines to recover and then store thorium.
Developing new extractants or synergistic systems to extract uranium in the presence of chloride;
Developing new solvent extraction systems to recover uranium from carbonate solutions.

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