URANIUM EXTRACTION
THE KEY ISSUES FOR PROCESSING

D Lunt\textsuperscript{1}, A Holden\textsuperscript{2}

1. Process Consultant, GRD Minproc Limited
2. Principal Process Engineer, GRD Minproc Limited

Presented by

David Lunt
David.Lunt@minproc.com.au

CONTENTS

1. ABSTRACT........................................................................................................................................1
2. INTRODUCTION...................................................................................................................................2
3. CONSIDERATION OF MAIN PROCESS DRIVERS ..................................................................2
4. ORE UPGRADING ..........................................................................................................................4
5. OVERALL CIRCUIT SELECTION – ACID LEACHING ..........................................................5
6. OVERALL CIRCUIT SELECTION – CARBONATE LEACHING .................................................9
7. LEACHING EQUIPMENT AND HEATING REQUIREMENTS ..................................................11
8. CONCLUSIONS ...............................................................................................................................13
9. REFERENCES ....................................................................................................................................13
1. ABSTRACT

This paper aims to pick up on the status of uranium extraction technology in the mid-80’s and raise possibilities for advancing extraction methods, reducing costs and transferring ideas and technology from sectors of the industry that have received greater focus in the intervening twenty years.

The key processing areas that are examined include:

- Pre-concentration by screening, gravity concentration and radiometric methods. A sacrifice in overall recovery can be offset by reduced capital expenditure on comminution, leaching and solid-liquid separation. Higher downstream solution tenors can also reduce the costs of primary separation using ion exchange (IX) or solvent extraction (SX).

- Leaching reagent costs. Lixiviant consumption and cost is a key element in the operating costs of both acid and alkaline leach circuits and particularly the latter. Whilst basic reagent consumptions are largely dictated by mass flow and gangue composition, judicious overall circuit design can cut the losses of leach reagent to tailings and improve project economics.

- Leach conditions. Leach kinetics can be slow for certain uranium minerals such as brannerite and davidite and carbonate systems are, in general, slower than acid systems. Higher temperatures can be employed to accelerate reaction rates and great advances have been made in autoclave technology in recent years.

- Heat energy input. Most uranium leach systems operate at elevated temperatures and, historically, little attempt was made to recover heat energy from leached slurries. Heat input is demonstrably the highest energy input into the majority of extraction circuits and there are gains to be made in recovering heat or at least minimising losses.

- Purification or separation of uranium in carbonate systems. Whilst it is possible to directly precipitate uranium from clarified leachate the presence of impurities such as vanadium, molybdenum and others may dictate that ion exchange is employed. Advances have been made in this area in terms of improved contacting equipment aimed at reducing resin inventories and hence costs.

- Separation in acid leach systems. This area has been a major focus of the industry in terms of optimisation, cost reduction and achievement of purer product. Developments of the 70’s included the use of combined SX-IX systems and the introduction of continuous counter-current ion exchange (CCIX). In the intervening period column SX has found a ready application to uranium in view of the rapid extraction kinetics.
2. INTRODUCTION

For over two decades the uranium industry has languished as evidenced by the dearth of new projects. This coupled with the closure of dozens of smaller operations has meant that uranium extraction technology has not advanced as rapidly as other areas of hydrometallurgy in terms of development and innovation. In a real sense the clock stopped somewhere in the early 80’s when the uranium bubble burst. National nuclear energy plans were drastically cut back in the USA, Europe and Japan, spurred by the Three Mile Island incident; the oil companies refocussed on core business and the spot price of uranium virtually halved from its mid-70’s peak. However, current price increases, buoyed by the likely acceleration of nuclear energy programmes, have led to a resurgence of interest in the metal. The focus of this paper is to examine the status of developments in processing technology in the mid-80’s and intervening years and to postulate areas of focus for new projects aimed at optimising designs and costs.

The objectives of any uranium recovery flowsheet, be it an alkaline or acid leach are to achieve high recoveries of the metal into an acceptably pure and marketable product and to achieve this in a cost effective manner. In discussing the equipment and flowsheet options available to the process engineer a number of these considerations are common to both acid and alkaline circuits. This paper deals with them as such and also discusses the key issues that are specific to acid and carbonate systems.

A somewhat greater focus is given in this paper to acid leaching than to carbonate on the basis that the former process is more common. In the 80’s approximately 14% of world output was obtained from alkaline leach projects and this has declined to zero at the present time. However, a significant number of new projects are contemplating this route and of course the Langer Heinrich uranium project, currently under construction in Namibia, has selected this technology.

3. CONSIDERATION OF MAIN PROCESS DRIVERS

3.1. KEY COST ELEMENTS

As a starting point for this analysis it is instructive to examine the major costs within a typical uranium extraction plant ie ‘within the fence’. EG Joe\(^1\) developed a breakdown of capital and operating costs for an acid leach circuit comprising the basic unit operations of comminution, leaching at elevated temperature, solid/liquid separation (CCD), Eluex (IX – SX), precipitation, calcining and packaging (refer to Figure 1). The analysis assumed a medium hardness ore with a relatively low acid consumption at around 20 kg/t. Cost breakdowns for such a system, in comparative terms, are given in the Tables 1 and 2 below.

<table>
<thead>
<tr>
<th>Table 1. Capital Cost Breakdown by Unit Operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process Area</td>
</tr>
<tr>
<td>Crushing/Grinding</td>
</tr>
<tr>
<td>Leach/Filtration</td>
</tr>
<tr>
<td>Eluex</td>
</tr>
<tr>
<td>Precipitation/Drying/(Packaging</td>
</tr>
<tr>
<td>Reagent Handling</td>
</tr>
<tr>
<td>Total</td>
</tr>
</tbody>
</table>

Whilst the above costs are generic, indicative and exclusive of environmental control and management it is clear that the major outlays are at the front end of the process ie in those areas where costs are heavily influenced by ore mass flows as opposed to uranium output. This confirms the potential advantages to be gained by pre-concentration of uranium as a capital reduction method.

<table>
<thead>
<tr>
<th>Table 2. Operating Cost Breakdown by Element</th>
</tr>
</thead>
<tbody>
<tr>
<td>Item</td>
</tr>
<tr>
<td>Reagents</td>
</tr>
<tr>
<td>Operating Labour</td>
</tr>
<tr>
<td>Operating Consumables</td>
</tr>
<tr>
<td>Maintenance Labour and Spares</td>
</tr>
<tr>
<td>Electrical and Heat Energy</td>
</tr>
<tr>
<td>Total</td>
</tr>
</tbody>
</table>
Of the operating costs the two most significant non-labour components are reagent consumption and energy input. This particular analysis revealed that more than half of the total energy usage of the process is expended in heating the pulp before and during the atmospheric leach process. The data point to the importance of minimising the key reagent consumptions (leachant, oxidising agent, ion exchange resin and SX extractant) and the steam usage in the leach circuit.

3.2. INFLUENCE OF URANIUM MINERALOGY ON THE FLOWSHEET

The type of uranium mineralisation and the nature of its association within a particular deposit will have a major impact on process route selection. It is convenient to classify ores into five types according to their processing characteristics:

- **Ores containing tetravalent uranium.**
  Tetravalent uranium has a low solubility in both dilute acid and carbonate solutions. To achieve economic recovery, oxidation to the hexavalent state is essential. Ore mineralogy can be oxide or silicate based. The silicates include uranothorite and coffinite which, having the zircon structure, would be expected to be refractory but, in practice, dissolve quite readily in oxidising acid or carbonate solutions. Oxidants include pyrolusite, sodium chlorate, Caro’s acid and ferric iron.

  The oxides have a simple structure and uraninite predominates. Low carbonate ores tend to dissolve fairly readily in acid solution with oxidant addition. However these oxides are often associated with carbonates and in these situations can be quite slow to dissolve demanding long leach times and possibly pressure leaching to achieve optimal recovery. Fine grinding may also be required with these ore types. Pitchblende is the massive form of this mineral and frequently occurs in veins.

- **Ores containing hexavalent uranium.**
  These ores are less common and usually of secondary origin. They are readily dissolved in dilute acid or carbonate solutions although an oxidant may be needed to prevent reduction through the presence of other species or ferrous iron introduced through grinding media. Carnotite, a complex of uranium and vanadium, is an example of such ores. Being oxidised it is often found in association with highly friable, clayey minerals such as calcrete and the associated solid/liquid separation issues are a key factor in process route determination.

- **Multiple Oxides.**
  These mineral species are complex and include associations of uranium with rare earths and the tin, tantalum, niobium, titanium family and, often, all three groups together. Their complex nature with extensive crystal lattice substitution means that they are highly refractory. This refractoriness increases with increasing niobium and tantalum content and decreases with increasing titanium, iron and uranium content.

  Examples of multiple oxides include brannerite and davidite and such ores were commonly encountered in the Elliot Lake region of Canada. These ores may require fine grinding, prolonged leaching in hot acid or even highly elevated temperatures in an autoclave.

- **Associations of uranium with carbon.**
  Ores associated with carbon may be classified as two types. Firstly uraninite can occur with fossil organic matter, possibly due to replacement. These may require fine grinding but otherwise are reasonably soluble in acid and alkali. Secondly, uranium can occur as a complex with organic matter, possibly humates. Being hexavalent such minerals dissolve readily. However, the carbon and organic matter can give problems downstream, for example in thickening and filtration and may interfere with phase separation in solvent extraction. In extreme circumstances such ores may require calcining.

- **Associations of uranium with phosphates.**
  Association with apatite is common. Although refractory, a proportion of the uranium will dissolve in the production of wet process phosphoric acid and is recoverable. Whilst the author has had considerable experience in this field, the extraction technology is relatively complex and is outside the scope of this paper.

3.3. ACID OR CARBONATE LEACHING

The presence of carbonate minerals in sufficient quantity to cause acid consumptions of greater than about 75 to 100 kg/t ore leached is likely to be the deciding factor in favour of carbonate leaching. This is equivalent to a calcite content in the ore of 7 to 10%. Higher acid consumptions may be justified if by-product metal species are present in economic quantities and where recovery from an acidic medium is simpler. The actual crossover point will vary by project and with reagent price hence projects need to be analysed on their own merits.
With the exception of the extreme condition described above, acid leaching is the flowsheet of choice. It evidences the following advantages over carbonate leaching:

- Faster leach kinetics than carbonate leaching of the same ore. This means that less aggressive leaching conditions can be considered (temperature, residence time) and a coarser grind size all of which give cost advantages.

- Since sulphuric acid is cheaper than sodium carbonate, it is not essential to recirculate the leachate following uranium recovery. In a carbonate system such recirculation is mandatory in order to conserve the leach reagents and achieve an economic outcome. The necessity for recirculation of carbonate in the alkaline leach system can rule out flowsheet options such as resin-in-pulp since solid/liquid separation is required in order to recirculate liquor. This issue also demands a focus on the overall project water balance as discussed later.

- Acid leach systems, whilst being intrinsically less selective over other metals, nevertheless have a much wider choice of downstream recovery and separation options. These can include ion exchange (IX), solvent extraction (SX) and combinations of these processes as in Eluex (or Bufflex as it was known in South Africa). The SX process exhibits the highest degree of selectivity for uranium over commonly encountered impurities. There are no solvents available for extraction of uranium from carbonate solutions and hence recovery methods are limited to IX or direct precipitation.

- In acid leaching the slurries tend to be less viscous than for carbonate systems and particularly carbonate systems associated with treating calcrete ores. In these circumstances the yield stresses of slurries can approach those encountered in nickel laterite slurry systems and can dictate that pulps be diluted to facilitate transport and agitation.

Against the above advantages of acid leaching, carbonate circuits do not need to employ acid resistant materials, except possibly in the precipitation circuit, and the carbonate leach is more selective. This latter advantage is, however, offset by the limitations on available separation technologies.

4. ORE UPGRADING

There is potential to upgrade ores ahead of both acid and alkaline and acid leach circuits and this factor should always be examined in the evaluation of a new project or the expansion of an existing one. A number of techniques are possible including:

4.1. UPGRADING BY SCREENING

Screening can be effective where uranium minerals report in significant quantities to the finer fraction of run of mine or primary crushed material. It has been applied in a number of situations and to a variety of uranium minerals. For example at Western Deep Levels the Venterdorp Contact Reef had a relatively low grade and only the finer fraction was subjected to uranium leaching with the balance reporting straight to the gold circuit.

The method finds particular applicability in the treatment of secondary minerals, particularly carnotite, in which the uranium tends to report with the fines. The Langer Heinrich uranium project will incorporate primary crushing and scrubbing followed by screening and rejection of essentially +0.5 mm material.

There is potential to apply technology that has been adopted in other industries, particularly nickel laterite processing, in terms of both equipment and unit operations. Consideration should be given to mineral sizers (where these are compatible with ore competency and abrasion indices), attritioners to enhance recovery and log washers to improve separation of clayey undersize from competent material.

4.2. UPGRADING BY RADIOMETRIC SORTING

Prior to the mid-80’s downturn in the uranium industry, radiometric sorting was beginning to make significant inroads into the flowsheet. Production units of the Ore Sorters Model 17 were installed at the Mary Kathleen, Western Deep Levels, West Rand Cons, Cenex and St Anthony mines. These units generally treated ore in size ranges between 25 mm and 150 mm. At the coarser end of this range throughputs of up to about 100 tph were being achieved.
Radiometric sorting is particularly applicable to vein type deposits where high grade mineral is discrete and easily separated from low grade material and gangue. The radiometric sorter at Mary Kathleen achieved recoveries of about 90% of the uranium in the sorter feed into 40% of the mass. The sorter product ran about 2200 ppm U$_3$O$_8$. The Kintyre project, also in Australia, and also a vein type mineralisation, had reportedly selected radiometric sorting as a means of pre-concentration before the project was shelved. Testwork indicated that this project was able to achieve very high upgrade ratios.

This technology must always be a consideration and especially so in situations where the downstream processing is likely to be more costly than the norm. For example, with refractory ores that demand long leach retention times or the use of high temperature autoclaves.

With the recent improvement in the price of uranium a number of the larger producers that now dominate the industry, are looking to radiometric sorting as a means of increasing output at existing facilities or maintaining output in the face of declining grades. A demonstration scale unit has been installed by Ultra Sort at Rossing Uranium (refer Figure 1) and will treat crushed feed in two size ranges between 80 and 300mm. Details of the installation have been published by Gordon and Heuer$^2$. Earlier units were controlled on the basis of a cut-point based on grades of product and rejects. Modern equipment has advanced in sophistication. Input and output tonnages and grades can be integrated such that the units can be controlled on the basis of the U$_3$O$_8$ upgrade ratio. This is particularly advantageous in situations where the mineralisation is fairly highly concentrated close to the economic cut-point and where a rapid response is required in the event of grade changes.

Figure 1. Rossing Radiometric Sorting Plant
Photo Curtesy of Ultra Sort

4.3. OTHER CONCENTRATION TECHNIQUES

Gravity concentration methods are not readily applicable to uranium minerals that are usually finely disseminated in the ores. A possible exception is uranium associated with pegmatites. Heavy median separation methods have been employed, most notably at Radium Hill in Australia where a -25 mm +10 # feed was concentrated ahead of leaching.

5. OVERALL CIRCUIT SELECTION – ACID LEACHING

The main circuit options for acid leaching are described in Figure 2. These tend to be driven by the choice of purification circuit that, in turn, has an influence on the selection of the solid/liquid separation unit operation utilised. Separation technologies include:
- Straight ion exchange. A variety of resin types are available and the contacting technology includes fixed bed (FIX) and continuous counter-current ion exchange (CCIX) and possibly resin-in-pulp (RIP). The CCIX technology has particular applicability to low $U_3O_8$ tenor solutions and designs appeared in the late 70’s engineered by Mintek, Davy (now Kvaerner) and Himsley. The advantages of the CCIX units over FIX included lower capital costs and a significant reduction in the resin inventory hence a lower operating cost. A further advantage of CCIX over FIX is that it is capable of handling unclarified solutions with, in practice, solids contents of up to 1-2%. The ultimate solids loading will be dependent on the size analysis of suspended solids.

- A more recent technology that seeks to achieve continuous (or at least semi-batch) operation and large reductions in resin inventory is the SepTor contactor developed and marketed by Outokumpo/SepTor Technology. These units operate in a carousel arrangement (refer Figure 3) and are essentially multiple fixed beds. They therefore require a clarified feed. They have an increasing track record across a range of industries and have succeeded in achieving the main objective of a low resin inventory.

- Solvent extraction (SX). The ubiquitous extractant is tertiary amine that supplanted the cationic D2EHPA systems in the 50’s. The anionic reagent has a greater selectivity for uranium than strong base resins and even the more selective weak base resins. A wide variety of equipment is available to the engineer including various designs of mixer-settler and SX columns. The latter contactor is particularly applicable to uranium SX where the extraction kinetics are extremely rapid.

- Eluex (Bufflex in South Africa). This system combines the ion exchange and solvent extraction operations into a sequential system. It can achieve greater selectivity than the individual processes.
The selection decision will usually be driven by one or more of the following factors.

**Figure 3. SepTor Carousel IX Unit**
Photo Courtesy of OKO/SepTor Technology

### 5.1. U₃O₈ LEACHATE CONCENTRATION AND PROJECT CAPACITY

From a chemical engineering viewpoint it is feasible to utilise any of the available purification routes described above. Theoretically all of the processes are capable of treating pregnant liquors of any U₃O₈ concentration. However, the optimum process route for a given set of conditions is not only a function of U₃O₈ tenor but is dependent on a whole range of interrelated factors, both technical and economic in nature. One of the major factors is the flowrate of pregnant liquor which has a significant impact on both capital and operating costs, particularly in the case of SX and FIX but to a lesser degree with CCIX.

The use of an Eluex circuit incorporating strong base resin CCIX followed by SX using mixer-settlers was shown to have a distinct economic advantage in the treatment of high solution throughputs. Studies undertaken by Brown and Hayden indiced that this configuration of Eluex is potentially superior to other options for pregnant liquors of less than about 0.35 g/L U₃O₈ and flows exceeding about 500 m³/h. However, the industry has not always agreed with this conclusion and has constructed direct SX plants employing conventional mixer-settlers having capacities in excess of 700 m³/h. With the advent of column SX and the economies that these contactors can achieve, with respect to both capital and operating costs, it is certain that the crossover point in terms of plant throughput will have moved even further in favour of direct SX over Eluex.

In the treatment of pregnant liquors having high U₃O₈ concentrations the SX route will, in any event, become progressively more attractive and would undoubtedly give superior economic returns at tenors greater than 0.9 g/L U₃O₈. This can be explained by the fact that full advantage of CCIX as a cheap uranium pre-concentration step is not realised unless significant reductions in the size of the downstream SX are achieved. This pre-concentration ability of CCIX is limited by two factors i.e.:

- The maximum concentration of U₃O₈ that can be achieved in the CCIX eluate. Historically plants have operated with eluates in the range of 4 to 7 g/L U₃O₈.
- The loading capacity of amine extractants has an upper limit of around 8 to 10 g/L U₃O₈ beyond which phase separation problems can arise.

### 5.2. SELECTIVITY

Acid leach purification processes can be ranked in order of decreasing selectivity as follows:

Eluex > SX and weak base IX > strong base IX

Strong base IX is the least selective acid leach purification process and with the trend towards tighter specifications for impurities is very likely to be unsuitable unless used as the initial operation in an Eluex process or in association with a very selective final precipitation process such as hydrogen peroxide precipitation. It is noteworthy that the Beverley Uranium project in South Australia has adopted this circuit configuration employing strong base FIX as the main extraction process.
The project has also adopted in-situ acid leaching. The large inherent resin inventory of the fixed bed process is better able to cope with the wide fluctuations in pregnant liquor $\text{U}_3\text{O}_8$ tenors that arise from this type of operation.

Weak base IX and direct SX have comparable selectivities and are usually capable of achieving nuclear grade uranium on their own. Weak base IX does, however, suffer from severe silica fouling were this species is present in the leachate and this has severely limited the application of this resin.

Eluex is the most selective of all processes combing the selectivities of both IX and SX.

A great deal could be written about the ability of the various processes to deal with impurities. It is instructive to summarise the ability of the SX and IX processes to reject the commonly encountered impurities. This is done in Table 3:

<table>
<thead>
<tr>
<th>Impurity</th>
<th>SX Separation Technique</th>
<th>IX Separation Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanadium</td>
<td>Reduction to the tetravalent state prior to SX&lt;br&gt;Hydrogen peroxide precipitation of uranium&lt;br&gt;Thermal methods post uranium precipitation</td>
<td>Reduction to the tetravalent state prior to SX&lt;br&gt;Hydrogen peroxide precipitation of uranium&lt;br&gt;Thermal methods post uranium precipitation or salt roast of the main feed</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Separate U and Mo stripping circuits&lt;br&gt;Activated carbon adsorption of Mo&lt;br&gt;Reductive scrubbing&lt;br&gt;Use of secondary amines&lt;br&gt;Hydrogen peroxide precipitation of uranium&lt;br&gt;Prior precipitation from pregnant solutions</td>
<td>Prior precipitation from pregnant solutions</td>
</tr>
<tr>
<td>Arsenic</td>
<td>Crowd off during extraction&lt;br&gt;Low pH scrubbing after extraction&lt;br&gt;Precipitation from pregnant solution</td>
<td>Precipitation from pregnant solution</td>
</tr>
<tr>
<td>Silica</td>
<td>Use of Polyox to remove colloidal silica prior to SX&lt;br&gt;Scrubbing post the extraction step</td>
<td>Use of Polyox to remove colloidal silica prior to SX</td>
</tr>
<tr>
<td>Ferric Iron</td>
<td>Crowd off during extraction&lt;br&gt;Low pH scrubbing post extraction</td>
<td>Crowd off during adsorption&lt;br&gt;Selective precipitation from eluates&lt;br&gt;Reduction to the ferrous state prior to IX&lt;br&gt;pH adjustment prior to IX</td>
</tr>
</tbody>
</table>

5.3. ABILITY TO DEAL WITH CHLORIDES

This issue is of relevance to any project contemplated in Western Australia and other parts of Australia that have highly saline water. Chloride anions, as would be expected, load readily onto the tertiary amine indeed the chloride ion is more strongly extracted than the bisulphate anion. The result is competition for active extractant sites with the uranyl sulphate complex. Cognis has observed that the presence of 2.5 g/L Cl$^-$ in Olympic Dam pregnant liquor (derived from the sodium chlorate oxidant) reduces uranium loadings by as much as 20%. The level of chloride in waters of the Eastern Goldfields region can be 50 times higher than this.

For projects faced with this issue, a possible solution could be to employ an Eluex circuit with a cationic resin (aminodiacetic acid type) employed in the primary extraction stage. This resin, of which a number are commercially available, extracts uranium as the cation ($\text{UO}_2^{2+}$) preferentially to anionic species including chlorides. The resin can then be stripped with dilute sulphuric acid and the uranium re-extracted selectively using SX. Such a system was contemplated in the early studies for the Key Lake uranium project.

A similar system might be contemplated using D2EPA (the Dapex Process) SX. As noted previously this extraction technique was employed prior to the commercial development of tertiary amine solvents.
5.4. LIQUOR PH AND OXIDATION POTENTIAL

Table 4 indicates the normal operational pH limits for the key unit operations:

<table>
<thead>
<tr>
<th>Process</th>
<th>Normal Feed pH range</th>
</tr>
</thead>
<tbody>
<tr>
<td>SX – Tertiary amine</td>
<td>&lt;1.0 to 2.0</td>
</tr>
<tr>
<td>SX – D2EHPA</td>
<td>&lt;1.0 to 1.8</td>
</tr>
<tr>
<td>IX – Strong Base</td>
<td>1.5 to 2.0</td>
</tr>
<tr>
<td>IX – Weak Base</td>
<td>1.5 to 2.0</td>
</tr>
</tbody>
</table>

The tertiary amine SX process is potentially capable of treating feed solutions having a wide range of acidities. Feed liquors normally contain exclusively sulphuric acid in view of the competing nature of nitrate and chloride ions over the uranyl anion. Acidities can vary from about 3.0 g/L H₂SO₄ for pregnant solutions to as much as 100 g/L H₂SO₄ for eluates. The extraction coefficient for uranium is reported to decrease rapidly above the pH range of 2.0 to 2.5 and extraction becomes ineffective above pH 4.0.

If the pH of the leach liquor prior to the purification process is raised too high then ferric iron or other complexes (arsenic, phosphates and others) may begin to precipitate within the extraction section. In order to minimise operating costs (ie sulphuric acid and lime for neutralisation) the leaching operation should be operated at the highest pH that is compatible with a high extraction in both the leach and SX sections whilst ensuring that post leach precipitation does not occur.

The upper pH limit for IX is also set by precipitation considerations. Apart from the sulphate present in leach liquor in the form of metal sulphates, pregnant solutions contain large excesses of free sulphate and bisulphate anions. The relative amounts are pH dependent. The bisulphate anion has a stronger affinity for anionic resin than sulphate and, since at low pH the bisulphate species predominates, uranium adsorption will be impaired. Some operations, such as Elliot Lake and Rio Algom used to improve resin loadings by neutralising with limestone ahead of IX to raise the pH and lower the bisulphate concentration.

Uranium can exist in solution in both the tetravalent and hexavalent states with the normal occurrence being the latter. For the commonly encountered purification processes (amine SX, strong and weak base IX) it is necessary that the uranium be in the hexavalent state to ensure full extraction and this will be the case if the emf is in the range −400 to −500 mV. In the event that reducing operations need to be undertaken ahead of extraction, eg for arsenic removal using H₂S or vanadium removal using iron, then problems can arise. Again it is suggested that an approach to overcome this would be to undertake extraction of the UO₂⁺⁺ ion using a cationic resin that is capable of extracting uranium in either valence state.

On the other hand, operation at too high an emf can give rise to problems with degradation of solvents eg isodecanol to decanoic acid and tertiary to secondary amine. This will result in lower extraction coefficients, slower phase separation and a decrease in selectivity.

6. OVERALL CIRCUIT SELECTION – CARBONATE LEACHING

The major flowsheet options for alkaline uranium leaching are illustrated in Figure 4. The alternatives for extraction are essentially either direct precipitation from leachate or extraction via IX. The equipment variants for the latter process are basically similar to those for acid leaching and include FIX, CCIX and the recently developed SepTor carousel. The use of RIP will preclude recirculation of the leachant and is likely to be uneconomic or at least reduce the returns of the project dramatically.

The key operating cost in the alkaline leach circuit is carbonate consumption and hence this factor, along with the selectivity of the extraction circuit, are the key issues that need to be addressed by the engineer.
6.1. SELECTIVITY

The methods for handling impurities in IX systems are essentially similar to the methods advocated in Table 3. For direct precipitation of uranium from carbonate leach solutions then the methods given in Table 5 can be considered.

**Table 5. Precipitation from Alkaline Liquors**

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Separation Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanadium</td>
<td>Treatment of bulk precipitates:</td>
</tr>
<tr>
<td></td>
<td>- Thermal methods</td>
</tr>
<tr>
<td></td>
<td>- Dissolution and re-precipitation</td>
</tr>
<tr>
<td></td>
<td>Precipitation prior to uranium eg with FeSO₄ or PbSO₄</td>
</tr>
<tr>
<td></td>
<td>Precipitation with peroxide</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Bleed recycle solutions from the circuit</td>
</tr>
<tr>
<td></td>
<td>Adsorption onto activated carbon</td>
</tr>
<tr>
<td></td>
<td>Precipitation of ferric molybdate</td>
</tr>
<tr>
<td>Sodium</td>
<td>Dissolution of sodium diuranate and re-precipitation</td>
</tr>
<tr>
<td></td>
<td>Use of hydrogen peroxide precipitation</td>
</tr>
<tr>
<td>Silica</td>
<td>Dissolution and re-precipitation</td>
</tr>
<tr>
<td></td>
<td>Modify leaching conditions</td>
</tr>
</tbody>
</table>
It is unlikely that direct precipitation from carbonate liquor will produce a marketable product without resorting to re-dissolution and re-precipitation or the use of more selective precipitation techniques such as hydrogen peroxide precipitation of uranium peroxide. This last method is selective over impurities such as vanadium which is commonly associated with secondary uranium mineralisation.

6.2. SODIUM CARBONATE CONSUMPTION

This is arguably one of the most critical factors in establishing a viable flowsheet whether this be direct precipitation from leachate or recovery from an ion exchange eluate.

With respect to a basic flowsheet incorporating CCD and IX (refer Figure 4), the circuit configuration must strive to maximise the input of fresh wash water (or tailings dam return water) to the final stage of the CCD. Unless this is achieved then soluble carbonate/bicarbonate will report to the tailings dam with the final CCD underflow. Depending on the percentage return of tailings solution to the process, this can lead to a significant reagent make-up cost.

The following options can be considered as a means of maximising the amount of water that can be used as CCD (or belt filter) wash:

- Recirculate a portion of the IX barren solution for use as mill circuit water addition. Interpose a thickener between the mill and leach circuits and recirculate thickener overflow to the mill,
- Utilise IX barren solution in the penultimate CCD stage as wash and use only fresh water as the final stage wash solution,
- Dissolve make-up sodium carbonate and bicarbonate in recirculating liquor as opposed to water or consider direct addition to the leach circuit as powder,
- Minimise the use of pump gland seal water around the process plant, and
- Consider indirect heat transfer instead of direct injection of steam into the leach tanks. However, this needs to be tempered by further consideration of slurry viscosity and the propensity for scaling of exchanger surfaces.
- Consider the use of belt filters as an alternative to CCD if filtration rates are favourable.

7. LEACHING EQUIPMENT AND HEATING REQUIREMENTS

7.1. LEACHING METHODS AND EQUIPMENT

The majority of leach circuits, both acid and alkali, have employed moderate temperature leaching in the range of about 40 to 70 °C and under atmospheric conditions. Leach temperature and residence time are determined from testwork aimed at optimising uranium extraction and reagent consumption.

In some circumstances it is beneficial to operate at elevated temperatures in autoclaves. These benefits can include:

- Oxidation of pyrite or other iron sulphides in the ore to generate sulphuric acid and ferric iron in order to dissolve uranium directly and more economically. The reactions are exothermic which is also an advantage. An example is the Afrikander Lease autoclave installation in South Africa.
- Increased dissolution of uranium in acid media where the ore is particularly refractory. Examples include the brannerite-containing ores of the Eliot Lake region. Rio Algom installed autoclaves ahead of pachucas to improve recovery.
- Acceleration of the reaction times for slow leaching ores. This has been the case with carbonate leaching of a number of ores. The Grants Mill of United Nuclear – Homestake, for example, employed a nest of vertical autoclaves (4.0m dia. by 5.0 m high) operating at 93 °C with 4.5 hours residence time to supplement the main leach and increase recovery.
- Reduction in reagent consumption particularly in acid leaching circuits where iron or iron/arsenic is directly precipitated in the autoclave. This, along with improved uranium recovery, was a driver for the use of pressure leaching in the Key Lake situation.
In non-pyrite pressure leaching of uranium, as in the leaching of nickel laterites and bauxite, it is advantageous from an energy usage viewpoint to utilise flash steam to preheat the autoclave feed slurry. The number of flash and heater stages is ideally minimised and, in practice, will depend on the volumetric throughput of slurry, the desired operating temperature and the maximum practical diameter of flash vessel.

Autoclave technology has made great advances in recent years with a large number of base metal and refractory gold reactors coming on-line. This is certainly an area where technology can be transferred between industries. The Macraes autoclave, illustrated in Figure 4 is an excellent example of a system that was constructed for a low capital outlay and that had a number of innovative features. These include the use of low cost pad style nozzles, Pyroflex membrane as opposed to lead, the use of CFD to determine and minimise autoclave shell thickness, the use of variable speed drives on the agitators and side entry flash letdown. The layout is organised specifically to provide access to high maintenance areas. This is well illustrated in Figure 5 where it is seen that there is ready access directly alongside the agitators, seals, nozzles and key instrumentation. The figure also indicates the positioning of the let-down valve on a mezzanine floor for ease of access and maintenance.

Figure 5 Macraes Autoclave

7.2. HEAT ENERGY CONSERVATION

As noted previously, more than half of the energy input into a typical uranium processing plant is supplied as heat to the leach system. For small to medium sized projects this heat is likely to be supplied from a boiler or hot water heater. Larger projects such as Ranger, Rossing and others have their own on-site acid plant that can generate steam via a waste heat boiler.

A number of earlier projects in South Africa and North America employed slurry-slurry heat exchangers to transfer heat from the hot exiting slurry to the incoming leach feed slurry. Randfontein Estates employed such a system at its Cooke uranium project. The concept is being employed on the Langer Heinrich uranium project with “top-up” heat supplied via a slurry-hot water exchanger. These systems need to have sufficient supplementary heat raising capacity to elevate the leach system temperature rapidly on start-up in order to maintain uranium recovery.

Again developments have taken place in recent times in the design of heat transfer systems for slurries. These include spiral and fluid bed exchangers.

It is also possible to transfer some heat energy to the incoming leach slurry without resorting to heat exchangers as would be desirable if the system were subject to severe gypsum scaling for example. This can be achieved by pre-thickening the leach feed and then back-diluting with a portion of the hot CCD overflow from the first CCD thickener.
8. CONCLUSIONS

The awakening interest in the uranium market must be seen as fillip to process engineers engaged in this field of hydrometallurgy. Whilst the uranium price of today is still (in constant 2006 dollars) a long way off the heady spot prices of the 1980’s the industry is once again on the move.

Hopefully this paper has provided some insight into the issues facing the process engineer tasked with flowsheet selection. Modern technology such as the Septor IX system, continuous pulsed column or sieve plate SX columns, autoclave systems and the latest generation of radiometric sorters will have their part to play as the upward trend continues.

The authors would like to thank the management of GRD Minproc in supporting the preparation of this paper and allowing its publication.

9. REFERENCES


